

# THE CONVERSION OF COAL INTO OILS

By DR. FRANZ FISCHER

*Director of the Kaiser-Wilhelm Institute for Coal Research, Mülheim-Ruhr;  
Professor at the Technical High School, Berlin;  
Member of the Reich Coal Council.*

AUTHORISED ENGLISH TRANSLATION

EDITED

WITH A FOREWORD AND NOTES

BY

R. LESSING

*PH.D.(MUNICH), F.C.S., M.I.CHEM.E., M.INST.P.T.;  
Consulting Chemist and Chemical Engineer;  
Honorary Secretary of the Coal Research Club.*

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## FOREWORD

THE problem of the production of oil fuel from coal was raised to a subject of first-class national importance for this country by the findings of the Royal Commission on fuel and engines for the Navy presided over by the late Lord Fisher in 1912-1913. The question became acute in view of the shortage of oil supplies during the war, and is being kept alive in Great Britain, and in other countries not producing natural oils, by the rapidly growing demands for liquid fuel for commercial purposes on land, on the sea and in the air. A fundamental condition for the solution of this question and the achievement of the still more ambitious task of the complete liquefaction of coal is a clearer and more precise knowledge of the constitution of coal, and of its behaviour under chemical and physical treatment, than we at present possess. Much progress in this direction has been made by workers in this country and in the United States of America during the last ten or fifteen years. An extensive series of valuable contributions to the subject has emanated from the Kaiser-Wilhelm-Institut für Kohlenforschung at Mülheim-Ruhr in Germany, a research organisation inaugurated in July 1914, a few days before the outbreak of the World War. The results of these investigations, carried out under the direction of Professor Franz Fischer and dealing with all phases of the production of liquid fuel from coal, have been published in six volumes of *Gesammelte Abhandlungen zur Kenntnis der Kohle* and in papers contributed to *Brennstoff-Chemie*. To most English readers these publications are known in abstract only. I therefore readily accepted Prof. Fischer's invitation to prepare an English version of *Die Umwandlung der Kohle in Öle*, a work in which the whole problem of the conversion of coal into liquid compounds is reviewed and critically examined in the light of his and his collaborators' researches and those of other workers.

In revising the English version the following questions had to be decided : whether additions to the literature on the subject published after the completion of the German manuscript should be dealt with ; whether the description of plant for low-temperature carbonisation, particularly in Great Britain, should be brought up to date ; and whether the author's expressions of opinion should be commented upon. In my endeavour to preserve the personal note of the book, and after consultation with the author, I decided to follow the original text without alterations, excisions or additions, as closely as is compatible with English phrasing. I considered it, however, desirable to append some notes dealing with the latest developments of low-temperature carbonisation, the treatment of primary tar and the hydrogenation of coals. The reasons for selecting the subjects of the additions are given in the Appendix.

The absence of general agreement on the question of the terminology of coal made it advisable to adhere to a literal translation of the types of coal used by the author, which are based in the main on the Westphalian classification.

## FOREWORD

The following approximate equivalents (with the terms of Seyler's present nomenclature in brackets) may be found useful :—

Lean coal	= dry non-caking coal ("carbonaceous");
Fat coal	= hard coking coal (meta-, ortho-, para-bituminous);
Gas coal	= long-flame caking coal (meta-lignitous);
Gas-flame coal	= long-flame non-caking coal (ortho-lignitous).

The generic term "bituminous coal" stands for *Steinkohle*, mostly as contrasted with "brown coal."

The actual translation, which other duties prevented me from carrying out, was made by Dr. H. Borns, to whom my thanks for much painstaking assistance are due.

I am also indebted to Mr. A. H. Raine for reading the proofs and compiling the index.

R. LESSING.

May 1925

## AUTHOR'S PREFACE

IMPRESSED with the scientific, industrial and economic importance of "the Conversion of Coal into Oils," I have written this book for the purpose of outlining the possibilities which the researches of the last decade have opened up.

Under the title adopted I have discussed both the partial conversion by cautious destructive distillation, with the "Production of Primary Tar," and the total conversion by direct "Hydrogenation of Coal," as well as the synthetic conversion preceded by gasification. The latter, the "Synthol Process," combined with primary tar production, likewise indicates the possibility of a total conversion, and indeed offers, in my opinion, the best promise for the future.

In order to complete and to frame the picture, I have added to the study of the three chief methods, which constitute the essence of the book, an introductory chapter on "Coal Extraction by Solvents" and a concluding one on "Hydrocarbons from Carbides." If the perusal of the book should suggest that my deductions seem to be based more upon work carried out under my direction than would appear justified from our share in the scientific output, the reader must not conclude that I underrate the importance of the work done elsewhere. I have, on the contrary, been anxious to give due consideration to all the literature on the subject. On the other hand, the investigations on which I have now been engaged for nine years have been planned and arranged to explore all avenues which lead from coal to oil.

I wish to express my indebtedness to my collaborator, Dr. Hans Tropsch, who kindly read the proofs and compiled the index.

FRANZ FISCHER.

MÜLHEIM-RUHR.



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## INTRODUCTION

The generation of power in stationary engines offers no difficulties in coal-producing countries. It is always possible to fire coal under boilers and raise steam for power purposes, or to gasify it and to use the gas as a heating or motive agent.

Limitations in weight and space, both as regards engines and the quantity of fuel required, influence the generation of energy for transport purposes, as on board ship, in motor vehicles or aircraft. So long as electrical energy in large bulk cannot be carried more efficiently than present-day accumulators permit, so long are we restricted to the use of liquid fuels of relatively high potential energy for motor propulsion. High calorific value, low specific gravity, freedom from incombustible constituents, small space occupied and many other advantages render liquid fuels indispensable for motor purposes.

Aircraft, motor cars and small boats call for low-boiling, commercial vehicles and large ships for high-boiling liquid fuels. The choice of fuel is determined by questions of fire hazard, type and speed of engine, the available space and permissible weight in the vehicle and other considerations. Sea-going vessels are not likely to be run on petrol, even at very low petrol prices, but on oils of higher boiling range on account of the smaller fire and explosion risk. In aircraft, on the other hand, motor fuels of very low boiling points and high calorific value must be used, as only these are suitable for light, high-speed engines, if a minimum weight per horsepower-hour is to be carried.

It is therefore not likely that either now or in the future a standard liquid fuel will be used, but different types will be required for different purposes.

The principal sources of liquid fuels are petroleum, and the gasoline frequently, but not invariably, present in natural gas. The latter and the low-boiling fractions of petroleum oil are petrol or benzine, the motor spirit of commerce. To these must be added the "cracked" spirits made by thermal decomposition of higher boiling petroleum fractions, produced particularly in America on a very large scale. The fractions of higher boiling range and the residue of the crude oil, in as far as they are not applied for lubricating purposes, find a use as fuel for oil engines of many types and for steam raising by direct oil firing.

There is a ready demand for the present very considerable production of petroleum. As regards low-boiling fractions, there exists a distinct shortage, which is made good by adapting engines to heavier fuels, by combining low- and high-boiling fractions and by other means.

The rapid development of motor transport makes countries not producing petroleum in more than negligible quantities dependent on its importation from abroad, but the shortage of crude oil, even in the most favourably situated countries such as the United States of America, is becoming more and more acute.

The world's oil production has experienced a tremendous development

## CONVERSION OF COAL INTO OILS

during the present century. Fig. 1 gives a picture of the magnitude and increase of the production of oil as compared with that of coal.

It shows that oil production has reached during the last few years one-tenth that of the coal mined, amounting to about 120 million tons of oil as compared with 1,200 million tons of coal.

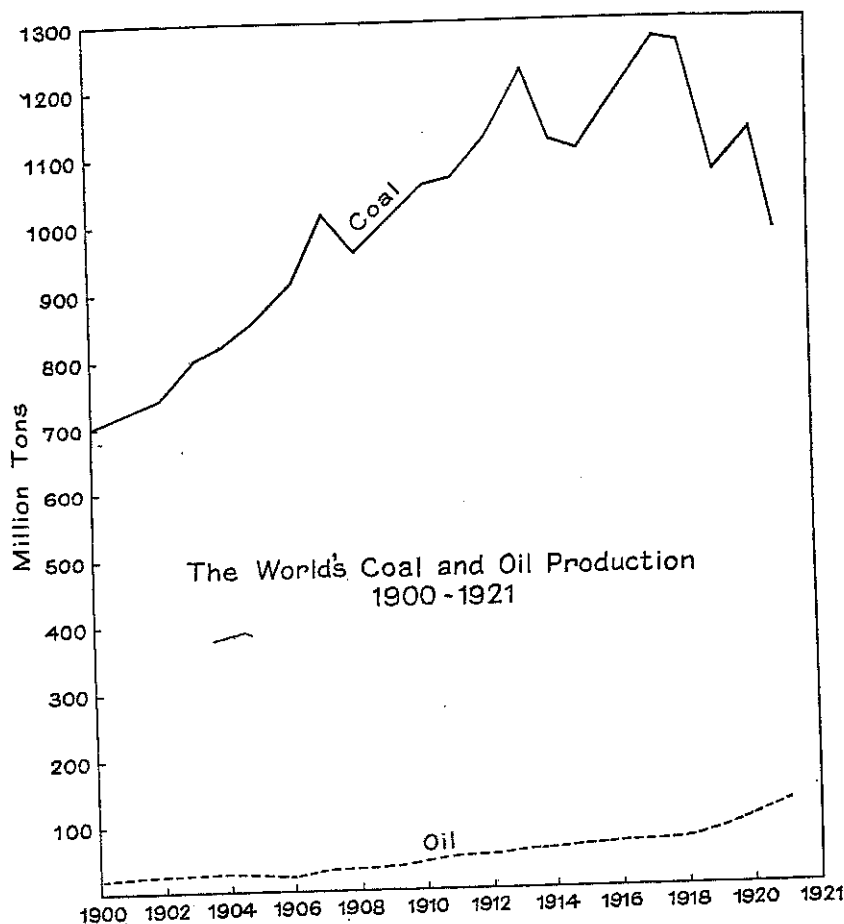


FIG. 1.

Fig. 2 gives a comparison of the quantities of oil and coal contributed by each continent during recent years.

Since 1900 Europe's participation in the world's oil production has receded to a minute fraction as compared with America. Even in the production of coal, Europe's contribution has considerably diminished and is already overtaken by America.

It is difficult to judge the duration of the productivity of oil wells or the additions to the existing production by drilling.

As any estimate of the visible and potential oil deposits must be largely based on guess-work, surprises must be expected in the future.

An estimate of the proved and probable coal deposits, on the other hand, is not quite so uncertain. An approximation of the coal resources of the world<sup>1</sup> is shown in Table I.

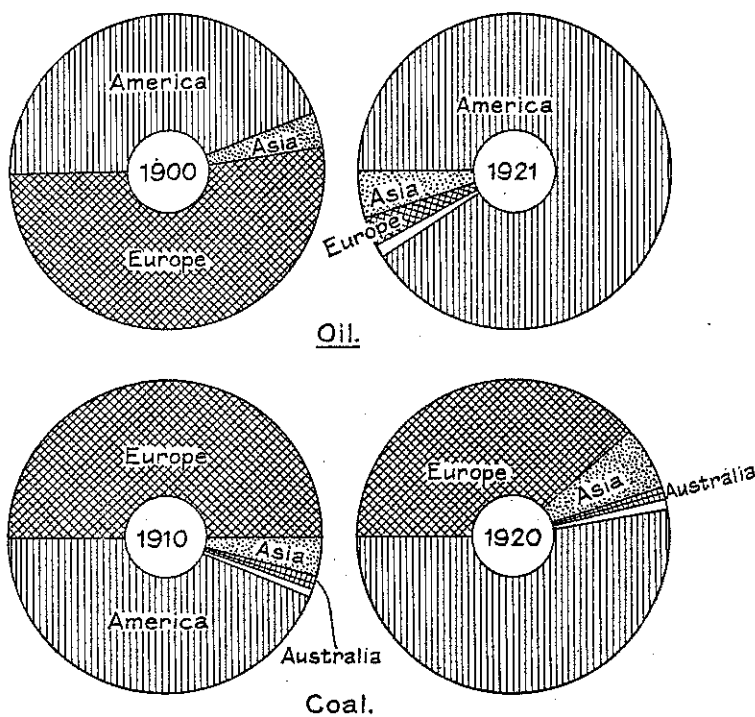


FIG. 2.—DISTRIBUTION OF OIL AND COAL PRODUCTION.<sup>2</sup>

TABLE I

	Total deposits, including proved, pro- bable and possible.	Proved deposits.
	Million tons.	Million tons.
Europe . . . . .	784,190	274,189
North America . . . . .	5,073,431	414,804
South America . . . . .	32,097	2,087
Asia . . . . .	1,279,586	20,502
Australia . . . . .	170,410	4,073
Africa . . . . .	57,839	500

The great advantages inherent in the possession of liquid fuel for the economic and political superiority of any country has led to keen competition for the control of the oil deposits of the world. It is to be expected that the victors in this struggle for oil are not likely to give up to other countries more than the surplus over their own requirements. These other countries are therefore forced to seek means by which substitutes can be found for petroleum, or for its components and products.

For this reason, Science and Industry have begun seriously to study the possibilities of a discovery of new sources and new kinds of liquid fuels, and to work out suitable chemical methods to this end. Disregarding the obvious certainty that new oil-fields will be successfully opened up, the most promising line of investigation seems to be the further development of those technical processes which even to-day yield liquid fuels not derived from petroleum.

The main sources of supply in this respect are gas-works and coke-ovens, the Scottish Shale Industry and the Brown Coal Carbonising (Schwel-) Industry of Central Germany.

An expansion of coking plants can economically take place only at the rate at which the demand for metallurgical coke increases. The same applies to gas undertakings and the increase in gas consumption. The production of tar oils and benzol as by-products of coke-ovens and gas-works is therefore not capable of unlimited expansion. The yield of benzol from existing plants could no doubt be increased by combining with the oil scrubbing plant, auxiliary absorption apparatus charged with activated charcoal or silica gel. Although such an increase in production would be valuable, it is still very small in comparison with the total requirements of low-boiling motor spirits.

The expansion of brown coal carbonisation is equally dependent on the ease and certainty with which the solid residue (Grude Coke) can be disposed of. The shale oil industry is hampered by the necessity of dealing with a large amount of incombustible solid residue, and the attempts at establishing it outside Scotland have hardly yet led to any success. No doubt in the two latter industries the yields of low-boiling spirit could be increased by improvements in the absorption plants. Moreover, the progress of oil shale distillation and brown coal carbonisation will depend on their capacity to compete with the petroleum industry in regard to cost of production, and finally on the supply of raw materials worth distilling.

In this connection it must be considered that as the result of technical progress certain deposits will be commercially workable which to-day cannot be treated at a profit.

One of the new possibilities for the production of liquid fuel on a large scale is low-temperature carbonisation, particularly of bituminous coal, a process which stands in close relation to shale oil distillation and brown coal carbonisation. The consideration of this process will form a large portion of this book.

Apart from coal as raw material for liquid fuel, some other possible sources must be mentioned. The use of alcohol as motor spirit is being widely investigated at the moment, in spite of its relatively low calorific value. Its production by fermentation from sugars, its recovery from the sulphite liquors of the paper industry, and its more or less direct production from wood are the most promising forms in which the solution of this problem is attempted. Its production is dependent on a liberal supply of vegetable materials, and one of the difficulties to be encountered is the collection of this material from vast tracts of land at costs which are not prohibitive. Calcium carbide is also suggested as raw material for alcohol.

Tropical countries are now considering the growing of oleiferous plants with a view to using the vegetable oils as liquid fuel, or to produce motor spirits from them by destructive distillation. Such processes may satisfy the local requirements of tropical countries to a limited extent, but are not likely to influence the larger problem of world supply to any considerable degree. Much more favourable are the possibilities for the production of liquid fuels in countries which possess sufficient coals, since Science has demonstrated the possibility of preparing all kinds of liquid fuels, and even the complete conversion of coal into oils.

The purpose of the present book is to consider this problem in detail, and particularly the following five methods :—

1. Extraction by solvents.
2. Production of primary tar.
3. Hydrogenation of coal.
4. Synthol process.
5. Hydrocarbons from carbides.

The second and fourth methods seem to be the most promising, particularly as they supplement each other and make possible the complete conversion of coal into heavy and light liquid fuels.

## CHAPTER I

### EXTRACTION BY SOLVENTS

#### (a) THE YIELD OF OIL BY EXTRACTION

If bituminous coal, brown coal, peat or oil shale are examined for pre-formed oil in the free state, in general only bituminous coal gives a positive result, and the recoverable quantity of oil is very small. The first solvent to be considered is anhydrous liquid sulphur dioxide.<sup>3</sup> It is advisable to dry the coal completely beforehand. During the extraction process, the coal swells somewhat and loses its cohesion. The extracted pieces of coal, after evaporation of the sulphur dioxide, fall to dust under slight pressure. The sulphur dioxide in contact with coal is quickly coloured yellow to orange. When concentrated, the solution is of dark claret colour without showing any fluorescence. After the removal of sulphur dioxide a dark red, heavy but limpid oil remains, from which a slightly fluorescent oil of agreeable petroleum-like odour can be recovered by steam distillation. The residue, not volatile with steam, contains other deep yellow compounds, boiling from 200° to 350°,\* which can be kept for years in air without visible alteration. A quantity of oil of not more than 0.5 per cent. of the weight of coal is recovered, and this extraction is therefore of no importance for the industrial production of fuel oil. It might assume some practical importance if these oils should be found to possess particularly valuable properties. In any case, liquid sulphur dioxide seems the only practicable solvent † for the purpose since it is cheap, and the requisite plant and technique have already been worked out by the Petroleum Industry for the Edeleanu process of oil refining. The oils which can be extracted from bituminous coal by sulphur dioxide are mainly hydrocarbons of wide boiling range, from benzine to lubricating oils and paraffin wax.

#### (b) IDENTIFICATION OF CHEMICAL COMPOUNDS IN THE EXTRACTS

The composition of these petroleum-like oils, which are contained in bituminous coal to the extent of about 0.5 per cent., has been studied by Pictet and his collaborators,<sup>4</sup> and later by F. Hofmann and Damm.<sup>5</sup> These workers used, however, other solvents and different coals. Fischer and Glud in their experiments with sulphur dioxide used a fat coal from the Ruhr District. Pictet extracted Loire and Saar coals with benzol, whilst Hofmann and Damm extracted an Upper Silesian coal with pyridine. On account of the difference in the coals, the hydrocarbons obtained have probably different composition. Pictet identified the following hydro-aromatic hydrocarbons: dihydrotoluene, dihydroxylene, dihydromesitylene, dihydroprehnitol and dihydrofluorene, with a number of naphthenes from  $C_8H_{16}$  to  $C_{13}H_{26}$ , hexahydrofluorene and

\* Unless otherwise indicated, all temperatures are in degrees Centigrade.

† Tetrahydronaphthalene being, under pressure in the autoclave at 250°, a powerful solvent, possibly hydrogenates coal, forming dihydronaphthalene or naphthalene.

melene, a solid paraffin wax-like hydrocarbon of m. p.  $62^{\circ}$  to  $63^{\circ}$ , to which he ascribes the formula  $C_{30}H_{60}$ . The boiling points of the hydrocarbons examined by Pictet range from  $100^{\circ}$  to  $300^{\circ}$  and many of them are identical with those found by Mabery in Canadian petroleum. F. Hofmann and Damm<sup>6</sup> also found several complete series of unsaturated and saturated hydrocarbons in their coal extracts.\*

The low-boiling members are missing; the unsaturated series begins at  $154^{\circ}$ , whilst no saturated hydrocarbons boiling below  $200^{\circ}$  were found. The unsaturated series runs from  $C_8H_{12}$  to  $C_{21}H_{26}$ ; the saturated, from  $C_{11}H_{20}$  to  $C_{24}H_{40}$ . Paraffins were found from  $C_{21}H_{44}$  to  $C_{27}H_{56}$ . Pictet found in the saturated oils only compounds of series  $C_nH_{2n}$ , but Hofmann and Damm observed higher derivatives, indicating the presence of polycyclic hydrocarbons in their oils. The densities of their unsaturated hydrocarbons differ also from those of Pictet's products.

A comparison of Pictet's results with those of Hofmann and Damm shows that many coals are impregnated with small quantities of petroleum-like hydrocarbons which differ in kind according to the type of coal investigated. It should be pointed out that Pictet, by establishing their optical activity, made the relationship of the hydrocarbons extracted from coal with those in petroleum still more probable.

It has already been stated that oil is not extracted by solvents at ordinary temperature from brown coal, peat and oil shale. They need therefore not be considered for the production of oil by extraction. The bulk of the bitumen in coal, and particularly that in brown coal (Montan Wax), peat, and oil shale, yield oil only by thermal decomposition at about  $400^{\circ}$ . The oil is, therefore, not a component, but a decomposition product of the bitumen,† and is only formed by destructive distillation.

\* Hofmann found phenolic constituents in the extracts, but "the data so far obtained are not sufficient to admit of definite formulæ with any degree of certainty."

† By bitumen is understood resin-, wax- and asphalt-like constituents which are extracted with organic solvents or decomposed on heating to  $400^{\circ}$  with the formation of oil (tar) and gas.



## CHAPTER II

### PRODUCTION AND WORKING-UP OF PRIMARY TAR

#### (a) METHODS OF DESTRUCTIVE DISTILLATION OF FUELS

DESTRUCTIVE distillation consists in heating the fuel to temperatures of several hundred degrees, when a few of the constituents pass over undecomposed, whilst the bulk of the material undergoes thermal decomposition, the gaseous and liquid products of which are to be found in the form of gas and tar. It will be understood that by the application of a considerable reduction of pressure a larger portion of the less volatile constituents can be recovered unchanged in the distillate. It is likewise evident that too rapid a distillation at ordinary pressure will, by superheating of the walls of the carbonising vessel, lead to a secondary and unnecessary decomposition of the products which have already passed into the gaseous state.

The vacuum distillation of coal has been studied by Pictet <sup>7</sup> in Switzerland, and by Wheeler <sup>8</sup> in England, almost at the same time. It was found that by the use of a vacuum some of the petroleum-like hydrocarbons present in coal, which Pictet had isolated by extraction, could be obtained as distillates. For commercial purposes vacuum distillation will hardly come into question, firstly on account of the cumbrous apparatus required, and secondly because the same product can apparently be obtained by distillation at ordinary pressure with the aid of superheated steam.

My collaborators, W. Schneider and H. Tropsch, <sup>9</sup> have investigated the vacuum distillation of lignite. They have found that, as against the liquid vacuum-tar of coal, a solid tar of as high a solidifying point as 53° is obtained, which consists of partly decomposed montan wax and a good deal of viscous oil. As regards the vacuum distillation of peat, little is known, but results similar to those from lignite are to be expected.

The distillation of fuels at ordinary pressure has been practised commercially for decades, on a very large scale, in gas-works, coke-ovens, shale and brown coal carbonising plants, not for the production, however, of a primary low-temperature tar ("Urteer"), but for other purposes. In all cases the desire for a rapid throughput, in view of the poor thermal conductivity of the fuel itself, is likely to lead to excessive heating of the walls of the carbonising vessel. There are also other reasons for this. In coking, the main object is to produce a firm and well-baked coke such as is required in the metallurgical industry. In gas-works the use of high temperature is dictated by the aim at the highest possible yield of gas. In the brown coal distilleries, again, which have hitherto mainly been worked for paraffin wax, there was no inducement to aim at a tar containing undecomposed montan wax, the parent substance of paraffin. Börnstein <sup>10</sup> has shown that distillation at very low temperatures yields tars which differ in their character from those obtained in the above-mentioned commercial processes. Together with my collaborators I

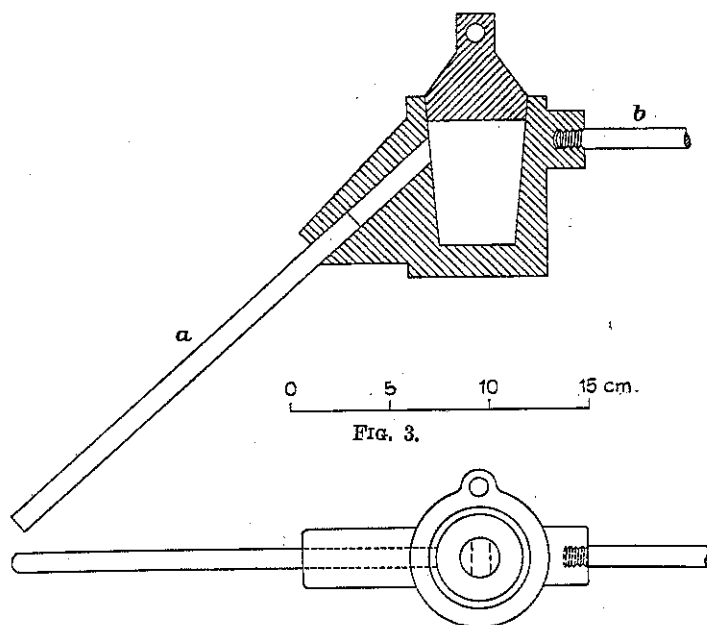


FIG. 3.

FIG. 4.

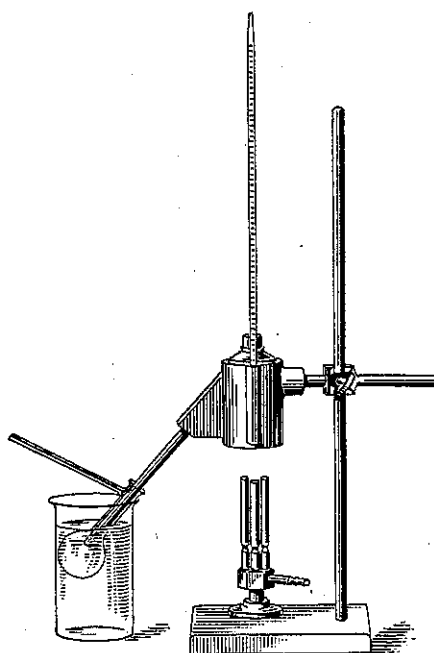
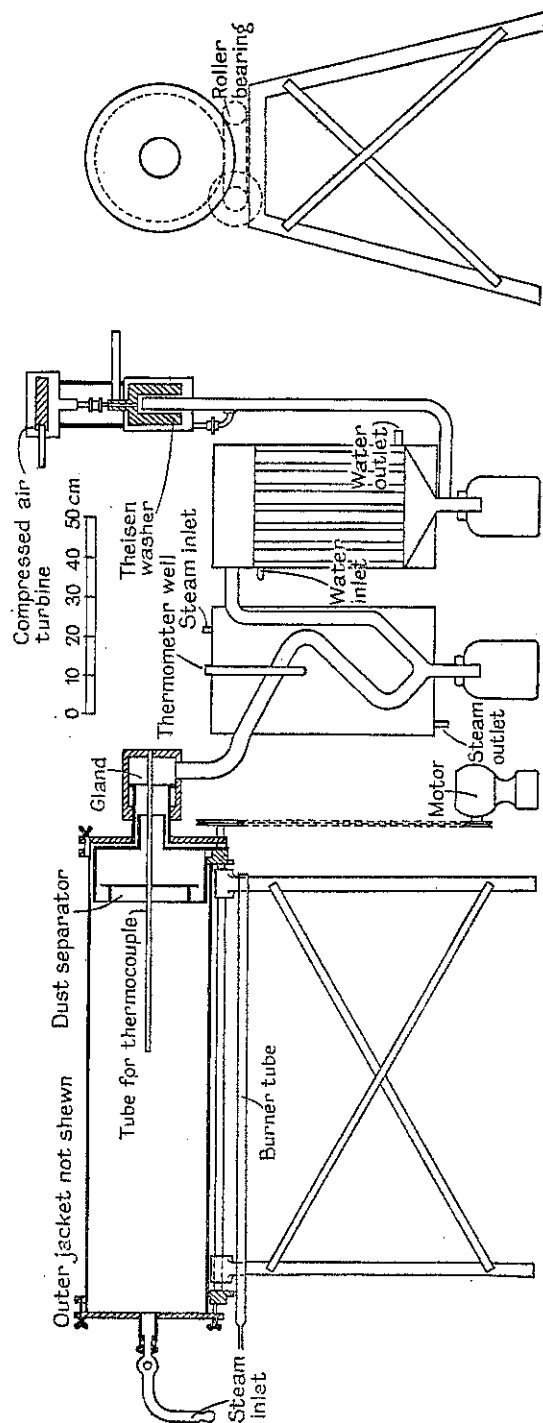


FIG. 5.



have resumed these little-noticed investigations, and have developed them in various directions. I shall revert later to the carbonisation of fuel at high temperatures.

(b) SPECIAL LABORATORY METHODS FOR THE PRODUCTION OF PRIMARY TAR

In order to produce oil by the carbonisation of coal, peat, or oil shale, it is necessary to reach the decomposition temperature ( $400^{\circ}$  to  $500^{\circ}$ ) of all the constituents capable of forming oils. It is advantageous not to raise the temperature beyond that absolutely required, so as to avoid any secondary superheating of the oil vapours, and even to cool the vapours as rapidly as possible to temperatures below  $300^{\circ}$ . Prolonged heating to higher temperatures would lead to the decomposition of valuable constituents with formation of gas and a consequent diminution of the oil yield.

For this reason methods of low-temperature carbonisation have been developed for the production of oil. The crude product of distillation containing the oil is called primary tar ("Urteer"). The gas which is always formed in the process contains the highly volatile oils (benzine).

These can be recovered by various means, such as washing with oil, compressing, cooling to low temperatures, or by treatment with activated charcoal.

For testing the suitability of fuels for oil production by distillation, the aluminium retort, illustrated in Figs. 3 to 5, is now frequently used.<sup>11</sup>

The apparatus consists of a cast, thick-walled aluminium crucible provided with a ground-in cover and outlet tube of special shape. The crucible is fitted with a lateral bore for the insertion of a thermometer or a thermo-couple. The high thermal conductivity of the aluminium and the thickness of the walls ensure uniform heating of the coal, avoid superheating, and permit an exact temperature control. The apparatus is made in different sizes, for 20, 50, and 100 grams of coal.

For the production of larger quantities of tar it is preferable to use the rotating drum, illustrated in Fig. 6.<sup>12</sup> It admits of performing the distillation without decomposition and in a current of steam.\*

The rotating drum consists of a cylindrical vessel made of sheet metal. It turns on rollers, is closed at one end by a screw cover, and takes a charge of from 10 to 20 kg. of coal. At the other end the cylinder is provided with a dust separator and a stuffing-box through which the gas and tar vapours pass to a condenser. The drum is heated by gas, and the temperature is measured with the aid of a thermo-couple. With a charge of 15 kg. of gas flame coal, the drum yields 1.5 kg. of tar in two hours. We have been working with a furnace of this type since 1916, and have examined by its aid nearly all German coals and many coals from other countries. We have also applied this apparatus to the study of brown coal, peat, and oil shales.

## (c) YIELDS OF PRIMARY TAR FROM COAL AND PEAT

The distillation of coal at the lowest possible temperatures, with a maximum of 450° to 500°, leaves a coke which contains practically the total nitrogen of the coal and about 10 per cent. volatile matter, *i.e.*, it still contains hydrogen compounds decomposable at higher temperatures with evolution of hydrogen. The tar and gas differ considerably from the corresponding high-temperature products. Tar is formed in much greater quantity and does not contain any aromatic compounds such as benzene, toluene, naphthalene or anthracene. The hydrocarbons of primary tar from all fuels resemble certain kinds of crude petroleum and are more or less rich in paraffin wax. Beside hydrocarbons, primary tars contain large quantities of phenols, which, with some kinds of coal, amount to more than 50 per cent.

Whilst the gas liquor in high-temperature carbonisation reacts alkaline owing to its ammonia content, the low-temperature liquor has an acid reaction,

\* The aluminium retort and rotary drum are supplied by Andreas Hofer, Mülheim-Ruhr, the mechanic of the Institute.

## CONVERSION OF COAL INTO OILS

as most of the nitrogen remains chemically bound in the semi-coke, from which it can, however, subsequently be recovered in the form of ammonia by further heating or by gasification. The gas from low-temperature carbonisation is rich in hydrocarbons, especially methane, and reaches a calorific value of 9000 calories per cb.m. (1000 B.Th.U. per cub. ft.).

TABLE II  
*Yield of Primary Tar from various Bituminous Coals*

Type of coal.	% Primary tar (dry).	Primary tar contains	
		Paraffin wax.	Phenols.
Lean coal . . . . .	abt. 1.5	?	0
Fat coal . . . . .	„ 3.5	1-2	15-20
Gas coal . . . . .	„ 8	1-2	abt. 30
Gas flame coal . . . . .	„ 12	1-2	„ 45
Cannel coal . . . . .	„ 29	?	5-10

Table II shows the yields of low-temperature tars from different coals. The figures refer to low-temperature tar free of water, and to dry coal. Percentages of paraffin wax and phenol are also recorded.

It will be seen that bituminous coals proper, from lean coal to gas flame coal yield more primary tar the younger and hence the richer in oxygen they are, and that the primary tars contain more phenols the younger the coal from which they were prepared. The content of paraffin wax in the tar from bituminous coals ranges from 1 to 2 per cent. Cannel coal, essentially of sapropelic and not ulmic character, stands in a class by itself. It is comparatively rare in Germany, but more frequent in England. High-grade cannel coals yield up to 30 per cent. of primary tar, which, as regards its paraffin and low phenol percentage, differs from the tar from bituminous coals and resembles somewhat that from lignites.

TABLE III  
*Yield of Primary Tar from different Brown Coals*

Kind of Coal.	Primary tar calc. for coal dried at 105°. %.	Primary tar contains		
		Paraffin wax. %.	Phenols. %.	Viscous neutral oils. %.
Saxon carbonising coal . .	24	29	15	17
Rhenish brown coal . . .	7.6	13	36	15
Lignite . . . . .	2.7	?	57	?

Table III relates to brown coals. Their higher paraffin wax and lower liquid phenol content is manifest from their pasty consistency at ordinary temperature. Unlike bituminous coal, brown coals give tars poorer in phenols and richer in paraffins as their total yield increases. This is clearly seen in Table III by comparing the Saxon carbonising coal with lignite.

In Table IV the yields of primary tars of different kinds of peat are recorded. The figures here vary as they do in the case of the lignites. The Lauchhammer peat, in particular, shows extraordinarily high tar yields.

TABLE IV  
*Yield of Primary Tar from different Peats*

Kind of peat.	Primary tar calc. for peat dried at 105°. %	Primary tar contains	
		Crude paraffin wax. %	Phenols. %
I. Fuel Peat from Velen (West-phalia) . . . . .	12	—	—
II. Lauchhammer Peat:			
(a) Top Layer . . . . .	18	14	14
(b) Middle Layer . . . . .	17	13	13
(c) Bottom Layer . . . . .	27	17	15

## (d) PROXIMATE COMPOSITION OF PRIMARY TARS

Fig. 7 gives the composition of the primary tar of gas flame coal in diagrammatic form.<sup>13</sup> It shows at a glance that approximately half the tar consists of constituents soluble in alkali,

mainly higher phenols and acid resins. The other half consists of neutral compounds and only about 1 per cent. of bases. On distillation at ordinary pressure, the constituents boiling above 300°, i.e., more than half the tar, would undergo a far-reaching decomposition. It is therefore advisable to distil in vacuo or with superheated steam. The first fraction of

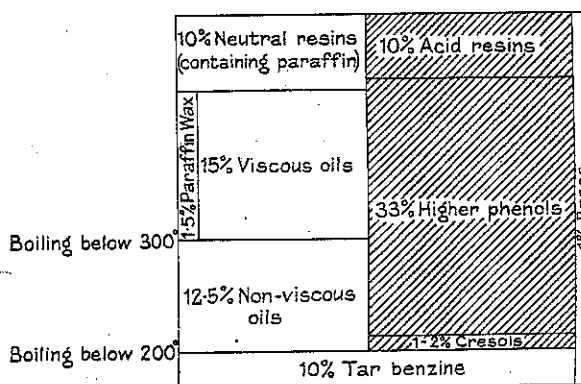


FIG. 7.

about 10 per cent. is tar benzine boiling below 200°. The phenols, having been previously separated, there follow limpid oils, viscous neutral oils and

neutral paraffinoid resins in three nearly equal portions. The viscous oils deposit, on standing, scales of paraffin wax amounting to about 1.5 per cent. of the total tar. The detailed composition of the hydrocarbons, phenols and bases will be discussed later on.

In primary tar from a Saxon carbonising coal, as shown in Fig. 8,<sup>14</sup> crude paraffin wax amounts to about 32 per cent. instead of 1.5 per cent. in the case of gas flame coal. On the other hand, the phenols amount to only about a quarter or one-fifth of those from gas flame coal. The proportion of the

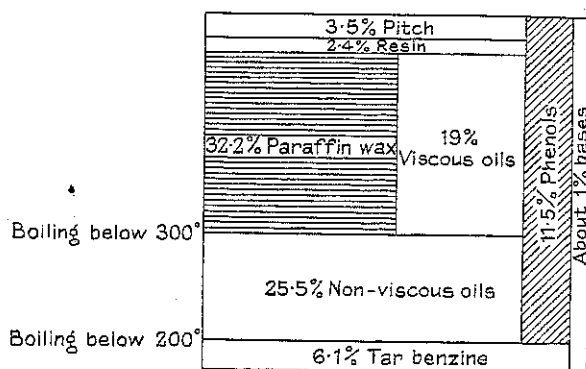


FIG. 8.

limpid neutral oils is roughly doubled; that of the viscous neutral oils is approximately the same. The percentage of bases is in both cases equally small.

#### (e) THE TEMPERATURES REQUIRED FOR THE PRODUCTION OF PRIMARY TAR

Various statements have been made on the behaviour of coal when gradually heated. Börnstein<sup>15</sup> describes the behaviour of gas flame coal from the Graf Bismarck Colliery as follows :—

About 200°	Water first split off
200–225°	First oily distillate
300°	Copious evolution of water
310°	First evolution of volatile sulphur compounds
390–400°	Main distillation commences
410°	First combustible gas
420°	Strong evolution of gas.

Fritsche<sup>16</sup> reports on the yield of primary tar at different minimum temperatures. He heated the aluminium retort (Figs. 3 to 5) charged with 20 grams of coal at a constant rate of 10° per minute to the desired temperature,

maintaining it until the evolution of gas ceased. Table V shows his results with Lohberg gas flame coal.

## TABLE V

*Lohberg Gas Flame Coal H<sub>2</sub>O 2.9%, Ash 11.0%; Used 20 grams; Rate of Heating 10° per min.*

Final temp. ° C. :	425	450	475	500	525	550	575	
Total yield of tar . .	1.15	1.94	2.10	2.42	2.40	2.45	2.43	g.
Water of decomp. . .	0.2	0.3	0.4	0.6	0.7	0.85	0.95	c.c.
Semi-coke . . . . .	17.62	16.48	16.11	16.46	15.20	14.83	14.65	g.
Primary gas (air-free), dry at N.T.P.	210	300	580	815	1060	1340	1440	c.c.

The bulk of the tar has come over at 450°, and the maximum yield is reached at 500°. Broche,<sup>17</sup> experimenting recently with a coal of the same origin, but less rich in tar, determined the periods required for securing the maximum tar yield at different temperatures. He heated the coal in the aluminium retort to a definite temperature and maintained it for a definite time. The experiment was then interrupted, and the tar yield determined. The figures of Table VI were thus obtained.

## TABLE VI.

*Tar Yields at different Temperatures according to Time*

Temp. ° C.	% After 20	% 45	% 60	% 90	% 180	% 240	% 300 minutes.
410	—	—	—	3.4	6.9	7.7	7.7
430	—	—	—	7.5	9.7	9.7	—
450	—	—	8.75	10.0	—	—	—
480	9.6	10.5	10.5	—	—	—	—
500	10.9	10.9	—	—	—	—	—

The table shows that down to 430° nearly the full tar yield is obtained, although the time required is ten times longer than at 500°. Nothing is known of the quality of these low-temperature tars, especially as regards their content of lubricating oils. Owing to the protracted heating they are not necessarily better than those obtained at 500°.

It should be pointed out that the heating periods at different temperatures relate only to the particular coal used, and that temperatures and duration of heating will vary for other coals, lignites and peats, according to their chemical composition. The examples show, at any rate, the course of tar formation at rising temperature and the minimum temperatures required for the highest



tar yield from bituminous coal. They further give the upper limit to which coal may be heated in rapid working to avoid tar losses by partial decomposition.

(f) DIFFERENTIATION BETWEEN VARIOUS PRIMARY TARS AND OTHER TARS

1. *Low-temperature and High-temperature Tars from Bituminous Coal.*<sup>18</sup>

The need has been expressed for some chemical criteria by which primary tars can be readily distinguished from ordinary tars. The characteristics given below may not definitely exclude the numerous varieties ranging from useless, solid and pitch-like producer tar to coke-oven tar, vertical retort tar, Mond gas tar and finally to low-temperature tar of high value, and there may be a need for a closer definition of true primary tar later on. The points specified below, however, will suffice as a guard against the crudest intentional sophistication.

(1) *General Characteristics.*

A good genuine primary tar \* from bituminous coal should satisfy the following general conditions :—

1. It should be fluid at room temperature, with possibly slight segregations of paraffin wax.
2. Its specific gravity at 25° should be 0.95 to 1.06.
3. In a thin layer it should be an oil of a golden-red or port-wine colour.
4. Freshly made it generally smells of hydrogen sulphide or ammonium sulphide; it should never smell of naphthalene.

(2) *The Naphthalene Test.*

These characteristics are, however, not sufficiently safe indications of a low-temperature or primary tar. To justify its name the low-temperature tar should have been produced by low-temperature carbonisation, i.e., it should not have been exposed to temperatures exceeding 550°, either during its formation or subsequently. A properly prepared primary tar *does not contain any naphthalene*.† Naphthalene is only formed secondarily from primary tar at temperatures upwards of 750°.‡ A tar containing naphthalene must therefore have been heated higher than the production of primary tar necessitated, and cannot rightly be defined as such. On this fact is based the simplest method of discriminating between primary and other tars. The higher temperature to which the naphthalene owes its existence changes the former in essential respects. The typical constituents of primary tar are paraffins,

\* By a good primary tar we mean a complete tar which still contains all the low- and high-boiling fractions.

† This fact was known to Börnstein. Having tested its accuracy we propose the naphthalene test for the discrimination of tars. Small traces have recently been found, but they are not shown by Fischer's test, which therefore holds good for the evaluation of a primary tar.

olefines, naphthenes and phenols, and only to a small extent aromatic hydrocarbons. To the first four types of compounds is due its low specific gravity. The conversion of these constituents into aromatic compounds, to which they are liable at temperatures above  $550^{\circ}$ , causes an increase in specific gravity. The latter fact provides a further means for distinguishing primary tar from tar which has been exposed to excessive temperatures.

For these reasons it is advisable to examine a tar which satisfies the general tests, but is still of doubtful low-temperature origin, for naphthalene, in the first instance. This is done in the following way: 200 c.c. of tar are distilled in a flask of 1.5-litre capacity in a moderate current of steam at  $100^{\circ}$ , the vapours being cooled in a very long Liebig condenser or two such condensers arranged in series, so that the distillate is perfectly cold. It is advisable to collect three separate fractions of about 250 c.c. each, which will all show a layer of oil on the water.

If the oil layer of one of the distillates solidifies to a crystalline mass, naphthalene is undoubtedly present, and the distillation may be stopped. In the case of a tar containing only a small percentage of naphthalene, the crystals appear only in the last of the three receivers or possibly only after cooling in an ice chest. The occurrence of naphthalene crystals unmistakably indicates that the tar has been exposed to too high a temperature and has consequently also been changed as regards other original constituents.

When subjected to steam distillation in this way, primary tar yields merely oily distillates, which will not show crystalline deposits, even after prolonged cooling in ice. By this test, additions to a genuine primary tar, of ordinary tar or inferior low-temperature tar containing naphthalene, can, of course, also be recognised.

### (3) *Determination of Density.*

In cases where naphthalene is found to be absent, a more detailed test is required.

Tar free of naphthalene is not always a primary tar, since superheating may not have been pushed to a point where naphthalene is formed, so that, though free of naphthalene, the tar has yet undergone some thermal decomposition. A method of distinction in such instances is based upon differences of solubility and specific gravity of the individual constituents. As already mentioned, the thermal history of a tar can be learned from the nature of its constituents and its specific gravity. The hydrocarbons offer a convenient means of studying these phenomena, whilst the phenols, on account of their varying proportions with different coals, are not suitable for this purpose.

The tar should first be shaken with petroleum ether in order to precipitate pitch and asphaltic matter. The solution in petroleum ether is then freed

of its acid constituents by means of alkali, and distilled up to 200°. The oils coming over from 200° to 300° are collected separately, and the specific gravity of the distillate and residue is determined. The specific gravity at 20° of the fraction from a primary tar, boiling from 200° to 300°, is below 0.95; in the case of other tars it is close to 1.0, or higher.

With a primary tar, the residue boiling above 300° solidifies to a pasty consistency, owing to segregation of paraffin wax; it is completely soluble in petroleum ether and in ether, and has at 50° a specific gravity below 1.0, *i.e.*, it will float on water of 50°. The corresponding residue from a superheated tar (although initially entirely soluble in petroleum ether) is, after distilling off the fraction 200° to 300°, only partially soluble in cold petroleum ether, leaving some solid matter undissolved. It is not completely soluble in ether and has at 50° a specific gravity above 1.0, *i.e.*, it sinks in water of 50°.

(4) *Examples.*

The following example may be cited:—200 c.c. of a commercial primary tar are vigorously shaken in a flask for a few minutes with 300 c.c. of petroleum ether (boiling from 30° to 65°). The solution, of a brownish-orange colour, is poured off the black, highly viscous deposit and is shaken in a separating funnel with 200 c.c. of 5*N*-sodium hydroxide. The aqueous layer is drawn off and is replaced by the same quantity of fresh lye, followed by further shaking and separation. The petroleum ether solution is now washed with an equal quantity of water and separated. It is filtered in order to remove any traces of water, and the petroleum ether is completely distilled off from a small flask on the water-bath. The residue is then freed of all constituents boiling below 200°, in a smaller flask resting on an asbestos plate. The residue is transferred to a still smaller flask of about 100 c.c. capacity and is distilled over a free flame up to 300°. The fraction boiling from 200° to 300° amounted to about 20 c.c.; the residue to about the same quantity. This mode of working was adopted for all the experiments summarised in Table VII and yielded the following data:—

TABLE VII

	Commercial primary tar.	Vertical retort tar.	Mond gas tar.
Spec. grav. at 20° of fraction 200° to 300°	0.9100	0.9850	0.9306
Spec. grav. at 50° of residue above 300° (determined in pycnometer) .	0.9606	1.0931	0.9713

The distillation residues from the primary tar and from Mond gas tar solidified to ointment consistency by the segregation of paraffin wax. Both were very readily soluble in the cold in ether and in petroleum ether; by triturating a sample with an equal volume of acetone the paraffin wax could be directly separated in the form of white flakes.

The residue from a vertical retort tar gave by comparison with the primary tar a negligible separation of paraffin in the form of a thin film; triturated with petroleum ether, it left a brown, insoluble mass. Ether left a very dark flaky mass undissolved.

#### (5) Discussion

On the strength of these distinctions it is no doubt possible to recognise by simple means how far any tar has undergone changes by subsequent heating, and to judge whether or not the product should be considered a true primary tar. To attempt to draw too narrow limits would not be advisable at present, in view of the variety of carbonising plant and of the coals used. The majority of tars should be distinguishable from primary tars without difficulty by the naphthalene test. It is therefore advisable to apply this test in the first instance.

The above-mentioned general characteristics of primary tar such as colour, etc., need, however, not be complied with in all cases. It may, for instance, occur that a primary tar is not liquid at the ordinary temperature. For if it was not separated by sufficiently energetic cooling, the low-boiling constituents which reduce its viscosity will be absent, and a pasty consistency will result owing to the separation of paraffin, although the tar still contains the valuable high-boiling lubricating oils. If high viscosity is caused by paraffin wax, the product should regain its fluidity at its melting point, 50°. The specific gravity of such a tar is naturally higher since the lighter constituents are absent.

(a) *Mond Gas Tar*.—The examination of a Mond gas tar proved that the general characteristic No. 3 may also be misleading, since the tar was quite black. The naphthalene test was, however, negative, and the tar could not have undergone any excessive heating. The figures for Mond gas tars in Table VII, for specific gravity of the distillate from 200° to 300° and of the residue boiling above 300° also indicated that it could be considered a primary tar which was merely devoid of the lighter constituents. To mistake such a tar, owing to the separation of paraffin wax and its pasty consistency, for a brown coal tar is hardly to be feared, since brown coal tars on account of their paraffinoid character have a much lower density than those from bituminous coal. In this case the general appearance did not characterise the product as a primary tar, although it had to be considered as the high-boiling portion of such a tar, still suitable for the recovery of lubricating oils; the

reverse case may occur of what appears to be a primary tar being really a high-temperature product.

(b) *Vertical Retort Tar*.—A case in point was that of a vertical retort tar from the Breslau Gas Works. The tar decidedly resembled in its appearance a good primary tar; it was of relatively low viscosity, did not smell of naphthalene, and a thin layer showed the characteristic golden-red colour. Here the density of 1.084, exactly as given by Lunge<sup>20</sup> for vertical retort tar, was at once decisive. The naphthalene test was, moreover, positive though the quantity of naphthalene found was small. The density determination of this tar, and further, its behaviour in petroleum ether, made it clear that this test allows of a definite discrimination, even in the case of a tar so closely related to primary tar as the vertical retort tar. This latter test, further, affords a means of estimating the high-boiling product of lubricating oil character; for it is conceivable that tars which have already been deprived of an appreciable proportion of these valuable compounds might make their appearance on the market. How far this test is generally applicable must be left to further experience.

## 2. *Distinction between Brown Coal Primary Tar and other Brown Coal Tars*<sup>14</sup>

Our present knowledge of the primary tars from brown coal is based upon the examination of tars obtained by low-temperature distillation in the rotary drum, from Central German brown coal and Rhenish lignite (Union Briquettes). Another primary tar was prepared from a lignitic brown coal from the Westerwald (Gewerkschaft Weiler I, Langenaubach). Of this tar, however (yield about 3 per cent. referred to dry coal), only the general properties were determined. We are, therefore, not yet in a position to say whether and to what extent lubricating oils were present in this tar. This tar differed, however, by appearance so widely from the others that it seemed not expedient on the strength of our present knowledge to define the general characteristics of primary tars from all varieties of brown coal. Whether or not this is at all possible will have to be settled by further practical experience with brown coal tars.

We have recorded for purposes of comparison the properties and results of some investigations of various brown coal tars. From these a few simple characteristics of really good primary tars are available for quick orientation. Table VIII is a summary of the results from comparative examinations of the following brown coal tars :—

(1) A primary tar from brown coal of the Riebeck Montanwerke, Halle, compared with a once-distilled primary tar and a commercial brown coal tar.

(2) A primary tar from Rhenish Union Briquettes and a once-distilled primary tar from the same coal.

(3) A good brown coal producer tar of the potash works Prince Adalbert A.-G. (Gewerkschaft Einigkeit II), Oldau.

For the sake of comparison a few data concerning the primary tar from the lignitic brown coal are added.

(1) *General Properties of Primary Tar.*—The primary tars from Central German brown coal and Rhenish lignite, as well as commercial producer tar, are products of the consistency of fairly hard butter. They have, therefore, all rather high setting points, upwards of  $+30^{\circ}$ ,\* whilst the commercial brown coal tar and the once-distilled primary tars have setting points far below  $+30^{\circ}$  (see Table VIII). The specific gravity of the tars offers no characteristic features, on account of the great variation in paraffin wax and phenol content. Sometimes one can obtain primary tars with much lower setting points from brown coal, as is shown by the examination of the primary tar from lignite, which has a setting point  $+12^{\circ}$ . Such a tar contains consequently little paraffin wax, as might be anticipated from the low bitumen content of the raw material. Whether such tar will be suitable for the production of lubricating oil remains an open question.

One rule holds for the primary tar from brown coal as well as for that from bituminous coal, viz., it must not contain naphthalene. The presence of naphthalene in the tar would indicate with certainty that a portion had been subjected to a temperature of at least  $750^{\circ}$ . Brown coal tars examined by the method previously described were free of naphthalene.

(2) *Examination of Hydrocarbons of Boiling Range  $200^{\circ}$  to  $300^{\circ}$  Soluble in Petroleum Ether.*—We first tried to follow the lines used for the discrimination between primary and other coal tars. It had been established that the fraction  $200^{\circ}$  to  $300^{\circ}$  of de-phenolised tar does not exceed a certain specific gravity, and this test answered in cases where the naphthalene test gave a negative result.

200 grams of tar were shaken for a few minutes in a stoppered bottle with 300 c.c. of petroleum ether ( $35^{\circ}$  to  $65^{\circ}$ ). If, as in the case of brown coal tars, the amount of insoluble residue was small, it was filtered off and washed with about 50 c.c. When, however, as with primary tar and producer tar, there was a large residue insoluble in petroleum ether, the solution was decanted; the tar was then again shaken with 200 c.c. of the solvent, filtered and washed with a further 50 c.c. The petroleum ether solution was

\* In the paper by Schulz and Kabilac, "On the Brown-Coal Generator Tar from Gas Generators" (Mitteilung des Industrieförderungsinstituts der Handels- und Gewerbekammer, No. 36, Prag, 1917) are given the setting points of generator tars from the gasification of various Bohemian brown coals, no exact origin being given. They range from  $+31^{\circ}$  to  $+34^{\circ}$  and correspond therefore to the primary tar from Rhenish brown coal in consistency. Spec. gravs. at  $50^{\circ}$  are from 1.002 to 1.015.

repeatedly extracted with 200 c.c. of 5*N*-caustic soda, washed with water, and filtered to remove moisture; the petroleum ether was then distilled off and the oil submitted to fractional distillation. The fraction boiling from 200° to 300° was collected separately and its specific gravity and that of the residue were determined. Table VIII shows that this course of examination was not completed in all cases. It is manifest that the specific gravity of fraction 200° to 300° does not discriminate between primary and other brown coal tar. It varies only from 0.859 to 0.895 in four samples and affords therefore no characteristic distinction. The same holds good for the residue after distillation to 300°. As it was noticed that the amounts of petrol-insoluble\* varied with different tars, the further examination of the tars at our disposal was based on this observation.

TABLE VIII

	Tars from central German carbonising coal.			Tars from Rhenish Union-briquettes.		Tars from lignitic brown coal.	Producer tar.
	1. Commercial carbonising tar.	2. Primary tar.	3. Once-distilled primary tar.	4. Primary tar.	5. Once-distilled primary tar.	6. Primary tar.	7. From Prince Adalbert potash works.
Setting point . .	+15/16°	+ 37°	+ 18°	+ 33°	+ 17°	+ 12°	+ 35°
Spec. grav. at 50° .	0.877	0.886	0.864	0.950	0.936	1.125	0.953
Portion of tar soluble in benzene and insoluble in petroleum ether	4%	47.5%	8.5%	35%	2.5%	not det.	37%
Spec. grav. at 20° of fraction 200° to 300° of portion soluble in petroleum ether and free from phenol and bases . .	0.874	0.859	not det.	0.890	not det.	not det.	0.895
Spec. grav. at 40° of residue above 300° soluble in petroleum ether	0.776	0.875	not det.	0.979	not det.	not det.	0.924

(3) *Differentiation of Brown Coal Tars by the Amount Insoluble in Petroleum Ether.*—Before the treatment with petroleum ether the tar (50 grams) was first dissolved in hot benzene (100 c.c.) and filtered hot to remove impurities, which consisted mainly of coal dust. It was then washed with hot benzene. The benzene solution was evaporated, the last traces of benzene being driven

\* Obviously unchanged montan wax and the like.

off in a vacuum on the water-bath. Twenty grams of the residue were well stirred with 20 c.c. of petroleum ether (35° to 65°) in a beaker and passed through a weighed filter. The insoluble residue was washed with 20 c.c. of petroleum ether, freed from adhering petroleum ether by drying at 100°, and then weighed. This procedure seems to afford a quick method for detecting a primary tar. Thus, the primary tar from brown coal gave, in the first instance, about 48 per cent. of residue insoluble in petroleum ether, but only 9 per cent. after having been once distilled. This is intelligible, as a primary tar is considerably decomposed by a single distillation, changing in consistency and in paraffinoid and acid constituents towards the ordinary brown coal tar with conversion of the montan wax into the more soluble paraffin wax. Of the commercial brown coal tars after purification with benzene, 5 per cent. were insoluble in petroleum ether. Similar results were obtained with a primary tar from Union briquettes, and the once-distilled product, the former containing 35 per cent. and the latter 3 per cent. insoluble. Judged by the residue insoluble in petroleum ether, the producer tar must therefore also be classed as a primary tar.

It is important to carry out this test under standard conditions and particularly with the same proportion of petroleum ether, since the solubility of the components is only relative. We have carried out a few more experiments with larger proportions of petroleum ether to elucidate these relations further.

Thus, 10 grams of a primary tar from brown coal, previously purified with benzene by treatment with twice the quantity of petroleum ether (20 c.c.) and washing with a further 20 c.c., gave altogether 35 per cent. insoluble in petroleum ether. In another case, 10 grams of purified primary tar from Union briquettes was treated with five times its bulk of petroleum ether (50 c.c.) and washed with 50 c.c. This yielded 15 per cent. of insoluble residue. Ten grams of purified producer tar from the Prince Adalbert potash works, having been mechanically shaken with 10 c.c. of petroleum ether for 1 hour, yielded a total of 30 per cent. insoluble in petroleum ether. These experiments indicate that the amount of residue insoluble in petroleum ether depends upon the proportion of petroleum used. Yet even where ten times the quantity of petroleum ether was used, the amount of residue was much greater than, for instance, the quantity obtainable from a once-distilled primary tar from Union briquettes which in its behaviour would approximate to a commercial tar from the same brown coal.

In conclusion, it may be stated that a brown coal tar which contains naphthalene is not a primary tar. If free from naphthalene it should be purified as described above by extraction with benzene, and after evaporating the benzene completely it should be treated with petroleum ether. Thus examined, primary tars from brown coal give more than 30 per cent. and



other brown coal tars less than 10 per cent. of products insoluble in petroleum ether.

3. *Differentiation between Primary Tar from Brown Coal and that from Bituminous Coal*

Primary tars from brown coal, leaving aside the special case of lignitic coal, differ from the primary tars of bituminous coal by their consistency. The latter, owing to their low paraffin content, are liquid (setting point  $3.5^{\circ}$ ), while the former are of semi-solid consistency (setting point above  $30^{\circ}$ ).<sup>21</sup> Benedikt and Bamberger, and also Franz Fischer and Tropsch,<sup>22</sup> have proved that bituminous coal is free from methoxyl, when examined by the Zeisel method for the determination of the methyl number, whilst brown coals contain methoxyl compounds.<sup>23</sup> This is recognised again in the primary tars. Thus, for instance, primary tar from bituminous coal was found free from methoxyl, whilst that from Rhenish Union briquettes contained methoxyl.<sup>24</sup>

(g) THE CHEMICAL COMPOUNDS FOUND IN PRIMARY TAR AND IN PRIMARY BENZINES

Most of the constituents of the primary tar have not yet been identified. Generally only those compounds are found which are already known from other sources; the unidentified compounds are apparently present in such complexity that their isolation has not yet been accomplished. The position is similar to that of petroleum, where, after many years of intensive research, only a few individual chemical compounds have been isolated, and these are often by no means characteristic of the petroleum because they frequently occur in negligible quantities. Coke-oven tar and lignite tar may also be quoted to exemplify how little such industrial products are really explored. In most cases only those products are known which obtrude themselves upon our attention by their particular behaviour; for instance, constituents which crystallise readily or are low-boiling, or which resist thermal decomposition. The more severely such tars are treated by heat, the fewer will be the surviving molecular aggregates. We know more concerning the low-boiling constituents of a tar than concerning the high-boiling, because the former are more easily disentangled, since in them the number of isomers is naturally smaller than in the higher boiling and highly substituted compounds. Hence primary tars, prepared by comparatively tender treatment and therefore retaining many labile constituents, offer particular difficulties to the elucidation of their constitution. To single out a few well-known and easily identifiable compounds is of little value for characterising a primary tar, unless their quantitative relation to the total tar can be proved. Unfortunately, some authors content themselves with the qualitative tests of

a compound, and thereby give the uninitiated a false impression as if the composition of a tar, or of a particular fraction, had been cleared up. Even if a narrow fraction, boiling, say, from  $79^{\circ}$  to  $81^{\circ}$ , is found to consist of 50 per cent. of benzene, that would not prove any appreciable occurrence of this compound in primary tar. For it is manifest that, if there were only traces of benzene present, these traces would accumulate at or about its boiling point. The proportion of the total fraction should be stated. It must, however, be admitted that the quantitative estimation of a compound in a highly complex mixture is more difficult than its qualitative identification.

In the following description of the various compounds so far identified, two further objections claim consideration. The aromatic compounds found may have been formed at too high temperatures by the dehydrogenation of products originally more or less hydrogenated. Further, where identified as sulphonic acids or as nitro-bodies, these compounds, during sulphonation or nitration, may have undergone oxidation to aromatic compounds. For these reasons it appears expedient to examine their density and other physical properties.

The opinion has been expressed that little is to be done chemically with the complex mixture, say, of the fraction  $200^{\circ}$  to  $300^{\circ}$  and that it requires, in the first instance, conversion by cracking into the less complex constituents of coke-oven tar. This can undoubtedly be done, but the proposal has no practical importance, for the primary tars are prepared in the first instance for power purposes, where their higher hydrogen percentage and complexity are of advantage. Density, boiling range, setting point and calorific value are here mainly decisive. Nevertheless, the exact scientific determination of individual compounds in primary tar is of great importance for their possible chemical utilisation. Such compounds, however, must first be discovered. The identification of single compounds is of subordinate significance for general characterisation, unless their quantitative proportions are known, or are negligible, whilst the main bulk remains unrecognised.

For this reason it should not be assumed that the compounds whose presence has been established or made likely by the workers cited below would give a true picture of the constitution of primary tars.

#### *Primary Tar from Bituminous Coal*

*Neutral Constituents.*—According to Franz Fischer and Gluud,<sup>25</sup> the fraction  $20^{\circ}$  to  $60^{\circ}$  of the benzine contains predominantly saturated and unsaturated members of the paraffin series. The fraction  $60^{\circ}$  to  $100^{\circ}$  presumably consists chiefly of members of the naphthene series and a few paraffins. This fraction resembles Russian benzine.

The fraction  $100^{\circ}$  to  $125^{\circ}$  is of too low a density to contain appreciable proportions of toluene, but it probably contains hydro-aromatic products.

The fraction 150° to 300° of the primary tar hydrocarbons contains about 10 per cent. of constituents not attacked by fuming sulphuric acid, the remaining 90 per cent. being olefines, partially or fully hydrogenated aromatic compounds and other hydrocarbons. The hydrocarbons boiling above 300° consist of solid paraffins and highly viscous oils. The composition of the solid paraffins lies, according to Gluud<sup>26</sup> between  $C_{24}H_{50}$  and  $C_{29}H_{60}$ , the members with 26 and 27 carbon atoms predominating. On the whole, the paraffin hydrocarbons, both liquid and solid, make up about 10 per cent. of the total fractions.

Schrader and Zerbe<sup>27</sup> found minimal quantities of naphthalene (0.01 per cent. of the total hydrocarbons).

In the neutral motor oil (200° to 300°) Weissgerber and Moehrl<sup>28</sup> found from 10 to 16 per cent. of paraffins and per-hydrogenated naphthenes, and from 50 to 60 per cent. assumed to be aromatic compounds by their solubility in sulphuric acid monohydrate. Of known compounds they found traces of naphthalene, and methyl- and dimethyl-naphthalene.

The unsaturated compounds have not yet been cleared up, though indene homologues are said to have been identified. Of aromatic compounds they identified pseudo-cumene, durene,  $\alpha$ -methyl-naphthalene,  $\beta$ -methyl-naphthalene, 1:6-dimethyl-naphthalene. As regards the naphthenes, the presence of per-hydrofluorene, per-hydroacenaphthene and deca-hydronaphthalene appears probable.

Weissgerber<sup>29</sup> found ketones of the open, non-aromatic chain type in the neutral fraction 190° to 200° of primary tar oils. He presumes the presence of more or less hydrogenated acetophenone.

Schütz<sup>30</sup> found in the benzines unsaturated hydrocarbons and acetone, in addition to saturated hydrocarbons (pentane), mercaptan and sulphides; in the neutral oil boiling above 75°, benzene, toluene, *m*-xylene, but no naphthalene. Part of the aromatic bodies was probably formed by dehydrogenation through superheating of the tar, or by dehydrogenation during the sulphonation tests. This opinion is, however, not shared by Schütz.<sup>31</sup>

Of saturated hydrocarbons he identified *n*-butane, *n*-pentane, methylbutane, methylpentane, hexane, heptane and octane; of unsaturated hydrocarbons, ethylene, propylene, butylene, pentene; of diolefines, 1:2- and 3:4-butadiene, *cyclo*-pentadiene, acetone, methyl-ethyl ketone, acetonitrile, methyl-mercaptan, dimethyl-sulphide and minimal quantities of carbon disulphide.

Morgan and Soule,<sup>32</sup> investigating the primary tar produced by the "Carbocoal" process (see p. 65), found that the neutral oils, remaining after removal of the tar acids and bases, are distinguished by their low density ( $D^{25} = 0.891$ ) and low viscosity. They confirmed the absence of noteworthy quantities of solid aromatic hydrocarbons upon cooling down to -30°. No

individual hydrocarbon was found in predominating proportion. The unsaturated hydrocarbons when present in considerable amounts cause on standing a gradual darkening and an increase in the density of the oil. Treatment with sulphuric acid of 98 per cent. strength left the saturated hydrocarbons behind. These consisted of about two-thirds naphthenes and one-third paraffins, totalling about 14 per cent. of the neutral oils. The unsaturated hydrocarbons, isolated for purposes of examination by means of liquid  $\text{SO}_2$ , belonged, as the determination of density, refractive index and molecular weight indicated, to the same series of cyclic partially hydrogenated hydrocarbons as those occurring in vacuum tar. Solid aromatic hydrocarbons were absent, but liquid members present in traces.

*Phenols.*—It has been proved that carbolic acid is present in very small proportions only.<sup>33</sup> The cresols are chiefly represented by *m*-cresol, the proportion of *p*-cresol is exceedingly small, but *o*-cresol is slightly more abundant. The distribution of the isomers is therefore quite different in primary tar from that in coke-oven tar. Like the cresols, the xylenols seem to amount to about 1 or 2 per cent. of the total weight of the primary tar. Concerning the higher phenols little information is available; only pyrocatechol has been estimated, approximately in a proportion of 0.25 per cent. of the total tar. Pyrocatechol is also known to be present in brown coal tar, but not in coke-oven tar.

Weindel<sup>34</sup> investigated the phenols of the tar from a "Tri-gas" producer. According to him the phenols of this tar consist only partly of a regularly ascending series of homologues, those higher than xyleneol being probably unsaturated in character. In addition, derivatives with more than one hydroxyl group are present, although in small quantities; they appear in the fractions from 240° to 275° (pyrocatechol). Among the higher members one may safely expect the presence of  $\beta$ -naphthol. Weindel did not isolate definite compounds, but he indicated the presence of homologues of cresol, viz. xyleneol, propylphenol, butylphenol, and amylphenol.

Morgan and Soule<sup>35</sup> established that their primary tar contained little carbolic acid, but considerable proportions of cresols and xylenols. Half of their phenols boiled below 220°. The cresols consisted of 27 per cent. of *o*-cresol, 19 per cent. of *m*-cresol and 54 per cent. of *p*-cresol. The isomers were therefore found in proportions quite different from other cases. Besides, the presence of xylenols was proved.

*Bases.*—Fischer and Gluud ascertained that the proportion of bases amounts to about 1 per cent. of the tar.

Gollmer,<sup>36</sup> investigating the bases of the tar from a "Tri-gas" producer, found little pyridine, but mainly bases of higher boiling point, the larger portion boiling above 240°. Referred to the proportion of hydrocarbons, the total amount of bases would be from 2 to 3 per cent., referred to the tar,

1 to 2 per cent. Apart from the symmetrical collidine, no definite compounds were determined owing to the complexity of the mixture.

Morgan and Souls<sup>32</sup> conclude from their investigation of the nitrogenous bases that 80 per cent. are tertiary and 20 per cent. secondary; primary bases were not found. The specific gravity of the mixture of bases was  $D^{15} = 0.993$ . Whilst in coke-oven tar bases quinoline predominates, they did not find any base preponderating in primary tar. The lowest boiling fraction contained pyridine, the higher-boiling bases have lower specific gravity and higher molecular weight than those of ordinary tar. They seem to contain partly hydrogenated nuclei and longer side-chains than the bases of coke-oven tar.

#### *Brown Coal Tar*

Graefe<sup>37</sup> states that the tar from brown coal boils from 150° to 400°, and consists essentially of liquid and solid members of the paraffin and olefine series. Among aromatic bodies he finds traces of phenol, cresol and substituted phenols to the amount of about 15 to 20 per cent. Marcusson has proved the presence of large quantities of ketones.

Ruhemann and Avenarius<sup>38</sup> found in the primary tar from a brown coal producer no carboic acid, but *m*-cresol and 1 : 4 : 5-xyleneol.

Fromm<sup>39</sup> established the presence of pyridine and considered that of picoline probable. Among the constituents soluble in alkali, carboxylic acids are only present in his tar in exceedingly small quantities. Of the phenols he could only identify *m*-cresol. Most phenols, of which he prepared urethanes, could not be identified with those already known. Apparently he had to deal essentially with unknown phenols.

Pfaff and Kreutzer<sup>40</sup> found thiotolene in the low-boiling fractions of ordinary brown coal tar which resembles the primary tar from brown coal, fraction 105° to 106° containing about 3 per cent. They further determined the presence of 2.2 per cent. ketones in the light oil from brown coal (100° to 200°), 3.3 per cent. of ketones in fuel oils (180° to 320°), and 4.5 per cent. of ketones in the dark paraffin oil (200° to about 400°).

On summing up the proportion of compounds definitely identified in primary tar, they are found not even to represent 10 per cent. of the total constituents. Matters are not much better in the case of the long-known coke-oven tar, the bulk of whose constituents have not yet been identified. The still unidentified portion probably consists of compounds of unknown constitution, hence the difficulty of their identification or isolation from the very complex mixtures.

## (h) THE LIQUOR FROM LOW-TEMPERATURE CARBONISATION

In addition to the oily condensate an aqueous liquor is obtained in low-temperature carbonising, partly due to the moisture in the coal, and partly to water formed on decomposition. To restrict the yield of liquor, in order to facilitate its removal or to allow of a more complete recovery of products from it, the coal should be dried before distillation. This is an essential procedure in the case of brown coal. This problem will be dealt with in detail in a separate section (p. 91). The gas liquor from low-temperature carbonisation reacts acid in the case of both bituminous and brown coal, and it differs in this respect from the coke-oven and gas liquors which react alkaline owing to their ammonia content. The acid reaction of low-temperature carbonisation liquor is due to the fact that in this process almost the whole nitrogen remains in the semi-coke, and that therefore only minute quantities of ammonia are formed. Since at low temperature more than the equivalent proportion of acid products is formed, the gas liquor contains the small amounts of ammonia in the form of ammonium salts, and in addition free acids.

The bulk of the ammonia appears only at temperatures between 600° and 800°, that is, above the temperatures used in these processes, and then in amounts larger than the equivalent of the acids produced in low-temperature carbonisation. Hence, in coke-ovens and gas works liquor the acids are neutralised by ammonia, and it contains in addition free ammonia and ammonium carbonate to which it owes its alkaline reaction.

Amongst organic compounds found in low-temperature liquor pyrocatechol may be cited in the case of bituminous<sup>41</sup> and brown coal. Methyl alcohol occurs in small proportions in the liquor from brown coal, whilst acetone has been found in small quantities in both cases. It would, however, appear that, at temperatures slightly higher than those strictly required for low-temperature carbonisation, the percentage of acetone is increased at the expense of other not yet identified bodies. This also applies to carbolic acid which, though contained in slight amounts in normal primary tar, is sometimes found dissolved in the liquor. The amount of liquor produced depends, as already mentioned, upon the moisture content of the coal. With dry coal, the yield of liquor wholly formed by decomposition equals that of the tar.

## (i) COMPOSITION AND APPLICATION OF LOW-TEMPERATURE CARBONISATION GAS

The yield of gas amounts with most coals to from 50 to 80 cb.m. per ton. There is a considerable difference between the low-temperature gas and ordinary coal gas, as shown in Table IX :—

TABLE IX

Primary Gas.				Crude Coal Gas.			
CO <sub>2</sub>	1-7%	H <sub>2</sub>	16-22%	CO <sub>2</sub>	2.0%	H <sub>2</sub>	50.0%
C <sub>n</sub> H <sub>m</sub>	3-5%	CH <sub>4</sub>	55-70	C <sub>n</sub> H <sub>m</sub>	3.75%	CH <sub>4</sub>	31.0%
O <sub>2</sub>	—	N <sub>2</sub>	3-4%	O <sub>2</sub>	—	N <sub>2</sub>	2.25%
CO	1-6%	H <sub>2</sub> S	4-5%	CO	9.0%	H <sub>2</sub> S	0.75%

The high percentage of methane hydrocarbons and the small percentage of hydrogen is characteristic for low-temperature carbonisation gas; further, unsaturated hydrocarbons predominate and may amount to 15 per cent. of the gas. Whilst coal gas contains benzol vapours, low-temperature gas contains benzine which is recovered in a similar manner to benzol. This product is designated "gas benzine" as distinct from "tar benzine" of a slightly higher boiling point, which in the dry distillation of coal is condensed together with the primary tar. Otherwise the distribution of benzine between gas and tar merely depends upon the conditions of the tar condensation. The more effectively the tar is cooled, the more benzine it will contain and the less will be found in the gas. According to various statements by practical men, the low-temperature gas of bituminous coal does not contain any hydrogen, and its yield is 150 cb.m. per ton. The former statement is certainly incorrect, for numerous reliable investigators have agreed in proving the presence of hydrogen in low-temperature gas from the most varied kinds of coal. The statement as to the gas yield is also open to doubt, and it will be desirable to settle this question, since the possible gas yield is of economic importance.

Table X, due to Foerster,<sup>42</sup> is interesting in that it illustrates the liberation of the various gases at rising temperatures.

TABLE X

Gas sample taken	CO <sub>2</sub> + H <sub>2</sub> S. %.	C <sub>n</sub> H <sub>m</sub> . %.	CO. %.	H <sub>2</sub> . %.	CH <sub>4</sub> . %.	C <sub>2</sub> H <sub>6</sub> . %.	N <sub>2</sub> . %.
up to 420° . . .	15.4	9.6	8.4	10.4	33.6	21.2	5.6
" " 500° . . .	6.2	4.6	6.2	24.8	40.3	14.4	5.7
above 500° . . .	5.0	2.2	5.2	34.3	41.4	6.8	6.2

The table shows that hydrogen makes its appearance below 420°, and that its proportion increases with rising temperature.

Similarly, Burgess and Wheeler found the following gases in an English coal :

	At 450°.	At 500°.
H <sub>2</sub> . . . . .	7.0%	16.6%
CH <sub>4</sub> . . . . .	25.0%	37.6%
C <sub>2</sub> H <sub>6</sub> . . . . .	34.1%	27.6%

Here also considerable evolution of hydrogen was observed even at low temperature.

In accordance with its composition, low-temperature carbonisation gas has a very high calorific value. Thus it has been established that the calorific value of low-temperature gas from bituminous coal, as prepared in the laboratory in the rotating retort, as free as possible from air, lies between 8000 and 9000 calories. Such values were obtained even when the gas had been stripped of its benzine vapours by washing with paraffin oil under pressure. In large-scale rotary retorts lower calorific values were obtained. This is due either to the production at the higher temperatures of a gas richer in hydrogen at the expense of the hydrogen content of the tar or semi-coke, or to leakage of air into the retort, which can scarcely be avoided in practice.

The gas from low-temperature carbonisation with its high calorific value can be used for many purposes. Compressed it may, for instance, be utilised for the illumination of railway carriages, since its calorific value is almost double that of ordinary coal gas. Gas holders of equal capacity, contain therefore at equal pressure twice the amount of energy, which means either improved illumination or a longer lighting period. In work of a lighter class it can be utilised in combination with oxygen for autogenous welding in place of acetylene. With a yield of 50 to 80 cb.m. of gas per ton of coal, *i.e.* only about a quarter or one-third of the yield of high-temperature gas, this valuable gas will easily find sufficient application. It will, however, not be used for heating the retorts as long as it can be otherwise employed. For this purpose gases of lower calorific power, like blast furnace gas or producer gas, are much more advantageous, since high temperatures are not only unnecessary but may lead to damage of the retorts or drums; moreover, these poorer gases are cheaper.

#### *Alcohols or Naphthenic Petroleum from the Unsaturated Constituents of Low-temperature Gas*

Various statements are found in the literature as to the possibility of the conversion of the unsaturated constituents of low-temperature gas such as ethylene and propylene, which may amount to 5 per cent. of the gas, into ethyl or propyl alcohol. The same problem has been investigated in relation to coke-oven gas for many years. The coke-oven gas is poorer in unsaturated constituents, and is therefore less suitable for the production of alcohol than low-temperature gas. Extensive experiments <sup>43</sup> have been made with concentrated sulphuric acid as absorbent, but in the coke-oven industry <sup>44</sup> no plant



seems to produce appreciable quantities of ethyl or propyl alcohol.<sup>45</sup> A similar process, however, is used in the American petroleum industry, where the gases from the cracking process which are rich in unsaturated compounds are treated with concentrated sulphuric acid. More recent researches<sup>46</sup> with coke-oven gas have shown that the absorption of ethylene may be considerably accelerated, not only by heating the sulphuric acid (95 per cent.) to 70°, but also by means of catalysts.

Damiens showed that sulphuric acid, on addition of 5 per cent.  $\text{Cu}_2\text{O}$  and some mercury absorbs ethylene very quickly with formation of ethyl hydrogen sulphate and diethylsulphate. From these products alcohol is recovered by hydrolysis with water.

If these catalysts are added to sulphuric acid, preheated until white fumes appear, or if  $\text{CuSO}_4$  and  $\text{Hg}_2\text{SO}_4$  are added, the acid will behave differently. It still absorbs ethylene at the ordinary temperature with extraordinary rapidity, but on standing after saturation, an oil boiling between 100° and 300° spontaneously separates. It consists of hydrocarbons approximately of the formula  $\text{C}_n\text{H}_{2n}$ , representing artificial petroleum formed by polymerisation from ethylene. Damiens does not give the yield of ethylene.

From the point of view of the production of liquid motor fuels from coal it is therefore possible, in principle at any rate, to produce from low-temperature carbonisation gas, or its unsaturated constituents, either ethyl and propyl alcohol or petroleum.

#### (k) THE LOW-TEMPERATURE BENZINE

It has been repeatedly pointed out that both brown coal and bituminous coal, on low-temperature distillation, yield, not benzol, but benzine. The possibility of obtaining benzine from bituminous coal is of particular interest. A gas flame coal from the Ruhr district (Fürst Hardenberg Colliery)<sup>47</sup> gives from 5 to 10 kg. of benzine per ton of coal comprising hydrocarbons boiling below 200°. 47 kg. of coal gave 130 grams of low-boiling benzine in the gas, and nearly double that quantity (270 grams) in the tar, or a total of 9 kg. per ton of coal. With coals of different origin the specific gravity of the benzine fraction boiling from 60° to 100° was about 0.72, similar to that found by Markownikoff for the benzine from Russian petroleum (Apscheron Peninsula), which for fraction 60° to 100° was  $D^{15} = 0.729$ . That the gas benzine from bituminous coal is an excellent motor fuel has already been established. Tar benzine should be refined before use.

These points have been investigated by Häusser,<sup>48</sup> of the Gesellschaft für Kohlentechnik. His gas benzine was obtained in the rotary retort plant of the Graf Bismarck Colliery, and had been stripped by the method used for extracting benzol from brown coal gas. The specific gravity of the gas

benzine was 0.794, the content of acid oils less than 0.5 per cent., and the boiling range was :—

76°	85°	90°	100°	110°	120°	130°	150°	165°
Drop	6%	11%	24%	43%	58%	72%	90%	95%

The spirit was therefore relatively high-boiling.

The benzine was tested on the bench in a 14/35 h.p. Audi motor engine, fitted with a Pallas carburettor, type SA III, and a 24 mm. air intake.

Häusser reports on the tests as follows : " The Audi engine was set for a compression ratio of 5.0, . . . the ignition 18 mm. in advance of the dead point. The air did not require much preheating; its average temperature was 82° before, and 37° after the carburettor. The slight preheating required assisted the efficiency. The temperature of the cooling water was normal. The carburettor was calibrated with

fuel nipple      No. 110 (i.e. 1.10 mm. diameter)  
 adjusting nipple No. 120 ( „ 1.20 „ „ )  
 by-pass nipple No. 110 ( „ 1.10 „ „ )

. . . The position of the brake blocks was not altered during the test. The results of the tests are summarised in Table XI.

" The behaviour of the fuel in the engine was satisfactory. It was easily started from cold and accommodated itself readily to quick changes in the load. There was no condensation in the suction manifold. The exhaust was perfectly clear at all loads and showed a slight colouring only on going to a heavier load. The sparking plugs remained white, and the valves were dry and free from deposit at the end of the trial. The results of the exhaust analyses are noteworthy. At all loads more carbonic acid and less carbon monoxide was found than had previously been observed with motor benzol III. The low-temperature carbonisation benzine is therefore readily and completely combustible as a motor spirit, as was confirmed by trials on the road."

TABLE XI  
*Primary Gas Benzine "Graf Bismarck"*

Revs. per min.	Torque mkg.	Eff. H.P.	Fuel consumption g./H.P./hr.	Per cent. by vol. in dry exhaust gases.		
				CO <sub>2</sub> .	O <sub>2</sub> .	CO.
1610	12.14	27.3	325	14.2	0.8	1.0
1500	10.79	22.6	342	13.9	0.9	1.2
1415	9.72	19.2	348	14.0	0.7	1.6
1310	8.30	15.2	364	13.7	0.8	1.4
1200	6.95	11.65	398	14.4	0.8	0.7
1110	5.87	9.1	446	14.2	1.6	0.6

Häusser concludes that the gas benzine made it possible to start the engine with ease from cold and enabled it to pick up quickly. The good pull of the engine, a feature not realised with motor benzol and certainly not with tetralin-benzol, was particularly striking. The inclination of petrol to pre-ignition and knocking is, according to Häusser, not observed in gas benzine from coal. This is shown by the fact that the compression ratio used for benzol could be maintained. Häusser ascribed the good performance of gas benzine in the engine to the greater hydrogen percentage and the more even boiling curve. He states :—

“ Whilst of motor benzol and benzol mixtures from 55 per cent. to 75 per cent. or more boil below  $100^{\circ}$ , the corresponding fraction of low-temperature gas benzine amounts only to about 25 per cent. If the boiling point of a constituent is taken as an approximate measure of its combustibility in the engine, it is found that low-temperature gas benzine contains an almost uniform series of constituents of ascending boiling points, each of which ignites the next higher one. This property is within limits more important than the boiling range, which does not differ much from that of motor benzol. The more even boiling curves account also for the good pull of the engine. The low-temperature gas benzines burn more quietly and yet with sufficient rapidity to ensure a satisfactory rate of combustion. On the other hand, the bulk of motor benzol burns fairly quickly so that the higher boiling and less combustible constituents get little chance for simultaneous combustion, and hence gives a poor pull.”

Benzines from bituminous and brown coal are, by contrast with the benzol products from coke ovens, very stable in the cold. The various fractions of coal benzine do not freeze, or give solid deposits at temperatures down to  $-50^{\circ}$ .

In the purification of the low-temperature gas benzines the most important point is the separation of the phenols and other acid constituents by means of caustic soda. This purification appears only to be necessary where the distillation has not been conducted with care, and the final boiling point lies above  $200^{\circ}$ . A further refining for the removal of unsaturated resinifying compounds is hardly required. The calorific value of the different fractions of a coal benzine (after purification) is approximately 11,000 calories.

Trutnovsky<sup>49</sup> reports on the gas benzines of brown coal. Brown coal from Styria was slowly distilled in the rotating drum, the gas obtained was passed through tubes charged with activated carbon, and the adsorbed benzine was subsequently liberated by the aid of steam. The benzine obtained had specific gravity  $D^{15} = 0.742$ , and gave the following fractions:  $23^{\circ}$  to  $46^{\circ}$ , 33 per cent.;  $46^{\circ}$  to  $80^{\circ}$ , 41 per cent.;  $80^{\circ}$  to  $100^{\circ}$ , 12 per cent.; residue above  $100^{\circ}$ , 8 per cent.; loss about 6 per cent. The yield of benzine referred to the low-temperature gas was 62 grams per cb.m., or 0.46 per cent. referred to dry coal.

The gas benzine from brown coal had an unpleasant smell and consisted essentially of unsaturated compounds, olefines and *cyclo*-olefines, and only to a small extent of paraffins and naphthenes. Trutnovsky considers, therefore, that the usual methods of refining and working-up should be discontinued in the case of these benzines, and that new methods will have to be worked out which will remove only the undesirable constituents.

(I) THE POSITION OF PRIMARY TAR BETWEEN COKE-OVEN TAR AND PETROLEUM

As repeatedly stated, the hydrocarbons of primary tar are more closely related to petroleum than to coke-oven tar, and particularly to oils which are mainly naphthenic in character.

The mixture of hydrocarbons in primary tar is optically active, as Fischer has established in collaboration with Gluud.<sup>50</sup> Optical activity has so far been found only in petroleum but not in coal tar.

The high hydrogen content of the light oils and benzine from primary tar is shown by their density, which, for products from many coals<sup>51</sup> and according to Broche<sup>47</sup> for unrefined benzines, agrees with that of Russian benzine.

The paraffin wax of the high-boiling fractions of primary tar, of which Gluud<sup>26</sup> determined individual constituents, is found in petroleum, but not in ordinary coal tar, which contains anthracene instead.

The proportion of benzene in primary tar benzine is quite insignificant, as Broche has once more confirmed by recent researches. It amounts to only a few per cent. in the fraction 60° to 100°. This is confirmed by the work of Frank and Arnold<sup>52, 53</sup> on commercial low-temperature carbonisation benzine, which also contains only minimal percentages of benzene.

A certain amount of benzene in petrol is, moreover, nothing uncommon. Engler's "Erdöl" gives several pages dealing with aromatic compounds occurring in petroleum.

Markownikoff<sup>54</sup> found almost 4 per cent. of benzene in the light oil fraction boiling below 105° of Russian petroleum from Grosny. This by no means puts this Russian benzine in a class with coal tar benzol. On the contrary, the resemblance of primary tar benzine to natural petroleum benzines is all the more emphasised. Reference to Engler's "Erdöl" will show the existence of very different kinds of petroleum of paraffinoid, hydro-aromatic (naphthenic), and largely unsaturated or aromatic nature.\*

With respect to the definition of a primary tar given by Gluud and myself

\* The presence of large quantities of unsaturated aliphatic hydrocarbons cannot be advanced against the likeness to petroleum. From Wietze crude oil 65 per cent. are dissolved out by conc. H<sub>2</sub>SO<sub>4</sub> (Engler, "Erdöl," 1, 274). For the unsaturated hydrocarbons in petroleum and their conversion into naphthenes see Höfer, "Das Erdöl," 4th ed. 312-313.

a few years ago, it should be understood that the naphthalene test must be carried out as described. The disclosure by more refined methods of the presence of minimal quantities of naphthalene, as we have ourselves first shown in our Institute,<sup>27</sup> does not disprove the petroleum character of the primary tar hydrocarbons. For naphthalene occurs in many kinds of petroleum, for example, according to Engler's "Erdöl,"<sup>55</sup> fraction 108° to 210° of Borneo petroleum contains 7 per cent. of it. In any event, as regards the significance of the naphthalene test, the statement on p. 32 must hold good.

The presence of true aromatic compounds in natural petroleum is an argument for the similarity between the hydrocarbons of primary tar and petroleum. Their quantitative estimation would alone be of value.

The physical properties, in particular the density of the hydrocarbon fractions, will always afford a ready guide for the distinction between mixtures of petroleum-like hydrocarbons rich in hydrogen, and coal-tar-like products, which are poor in hydrogen.

These considerations prove therefore that the hydrocarbons of primary tar are more closely related to those of petroleum than to those of coke-oven tar, which latter are predominantly aromatic in nature (benzene, naphthalene, anthracene and their homologues).

In contrast to coke-oven tar, carbolic acid, the phenol of lowest boiling point, is present in very small quantity in properly prepared primary tar. In addition to cresols and xylenols (see p. 27), mostly high-boiling phenol homologues are found, similarly to those which occur in certain petroleum (Engler, "Erdöl," 1, 434).

#### (m) SEMI-COKE

Bituminous coal, brown coal and peat leave on distillation a semi-coke, a kind of smokeless fuel containing from 10 to 15 per cent. of volatile matter. To the proper utilisation of this semi-coke much thought has been given, as it is mostly very porous and friable, and occasionally (especially in the case of brown coal) liable to spontaneous ignition even at low temperature.

The application of semi-coke as smokeless fuel, which was first tried in England, meets with considerable difficulties, for its friability and high porosity become very troublesome on handling and during transport. One might expect that on making the coal denser by compression, while still in the retort and in a plastic condition, a coke of better physical qualities should be obtained. With this end in view Parr and Olin<sup>56</sup> fitted a screw-actuated piston into a horizontal stationary retort, by means of which the coal rammed into the retort was compressed during carbonisation.

Parr and Olin succeeded in this way in raising the specific gravity of the outer portion of their semi-coke (which uncompressed had a specific gravity

of 0.65) to 0.73, an increase of 12 per cent. The core remained more porous. On the other hand it was to be expected that carbonisation with the application of external pressure would render the withdrawal of the tar and gases more difficult. I have succeeded in devising an astonishingly simple contrivance<sup>57</sup> which meets all requirements. When the rotating drum is used for intermittent distillation of the coal, a massive iron roll of about 10 cm. diameter, and somewhat shorter than the drum, is placed within the charge of disintegrated coal. Upon heating and revolving the drum, the coal, as it becomes plastic, cakes and forms a lining on the wall of the drum. The roll lying loose in the drum compresses the coal, the density increasing with the plasticity. When degasification is completed, the coke lining adhering to the wall of the drum begins to crumble and fall in. As the noise attracts attention, the rotation of the drum can be stopped at the right time. On opening, it is seen that almost the whole drum is lined with a uniformly dense layer of semi-coke. In a small-scale experiment I obtained, from 15 kg. of gas flame coal, 11.3 kg. of compressed semi-coke and 1.5 kg. of tar oil, or about 75 per cent. of semi-coke and 10 per cent. of oil. The semi-coke produced had an average density of 0.68, whilst without use of the heavy roll the density was 0.45. The increase in density would therefore amount to about 50 per cent. The determination was made by grinding pieces of coke to cubes exactly 1 c.c. in volume, and weighing them. The yield of crude oil was not influenced by the use of the heavy roll. The calorific value of the crude oil was about 8800 calories.

This semi-coke provides a dense smokeless coal quite fit for transport. Its properties are of vital importance for the economics of the process. The rolling-down of the semi-coke within the retort and during the detarring and degasification, which is characteristic of this process, is not directly applicable to continuous rotary retorts in which the coal is fed in at one end and the coke is taken out at the other end.

It was to be expected that the production of a compressed semi-coke would not be directly possible with all coals. The condition is that the coal softens while being heated, and this property does not exactly depend upon the amount of bitumen in the coal. It is known, of course, that brown coal, whether rich or poor in bitumen, will not cake. Yet it was conceivable that a compressed semi-coke might be obtained by blending non-caking and caking coals, or by adding certain substances in definite proportions yet to be determined.

Various experiments were made in this direction,<sup>58</sup> the results of which are summarised in Table XII. The coals were finely ground in a ball mill and were distilled without the aid of steam. Charges of about 10 kg. of coal, or coal mixture, were used. Distillation was stopped either when the noise of the dropping coke pieces was heard, or when the temperature in the centre of the drum (measured in the usual way) had risen to 525°, when, according

to our previous experience, the formation of primary tar was completed. In the experiments in which a compressed semi-coke was produced the maximum temperature was only about 450°, owing to the bad thermal conductivity of the coke lining formed.

TABLE XII.

Raw Material.	Moisture in coal. %.	Coal used.	Tar.	Coke.	Gas.	Coke quality.
Gas flame coal (Lohberg Colliery) Dinslaken.	1.2	10 kg.	8.4	76.92	not determ.	firm
Fat coal (Rheinpreussen Colliery).	0.6	10 kg.	2.5	87.52	564	„
Union briquette (Rhenish).	13.2	10 kg.	6.86	58.18	754	fine powder
Gas flame coal + Union briquette.	—	{ 5 kg. + 5 kg.	6.04	67.88	866	„ „
Gas flame coal + Union briquette.	—	{ 7½ kg. + 2½ kg.	8.82	72.54	846	„ „
Gas flame coal + Carbonising brown coal (Riebeck's Montan Works.	—	{ + 2½ kg.	11.91	68.09	776	„ „
Carbonising brown coal (Riebeck).	11.9	10 kg.	19.49	54.48	1037	„ „
Brown coal semi-coke + Brown coal tar.	—	{ 4800 g. + 4800 g.	not determ.		365	„ „
Brown coal semi-coke + Brown coal tar oxidised under pressure.	—	{ 3390 g. + 3390 g.	„	„	434	„ „

A gas flame coal (Lohberg Colliery, Dinslaken) and a fat coal (Rheinpreussen, Röttgersbank) both yielded a compressed, firm semi-coke which formed a crust on the walls of the drum and could be easily broken into pieces. The previous experiments were thus confirmed. With Central German brown coal rich in bitumen, and with Rhenish lignite (Union briquettes), not the slightest tendency of the semi-coke to caking could be observed. The coal was discharged in the same fine powdery condition in which it had been fed into the apparatus.

In order to ascertain how far addition of this gas flame coal to the lignite briquettes would influence the properties of the semi-coke, equal quantities of the two coals in finely powdered condition were well mixed and distilled in the drum. The coke residue obtained was a fine powder, and did not show the slightest inclination to caking. A good mixture of three parts of finely powdered gas flame coal and one part of finely powdered lignite briquettes

gave on distillation the same result. Central German brown coal, rich in bitumen, behaved likewise. Thus, even considerable excess of gas flame coal when mixed with brown coal did not lead to a caked semi-coke, such as the gas flame coal had given when distilled alone. In other words, even a relatively small addition of brown coal renders bituminous coal non-caking. Similar observations had already been made in practice and are applied in the gasification of bituminous coal in producers, where in order to prevent caking some brown coal is sometimes added, and this fact furnishes a good confirmation of the experience we gained in our roll experiments.

Two further experiments were made. Brown coal semi-coke was mixed in a kneading machine in equal proportions, in the one case with ordinary brown coal tar, and in the other with brown coal tar oxidised under pressure,\* and then distilled. In neither case caking took place. This was perhaps hardly to be expected with the addition of brown coal tar, in view of the experience with brown coal itself, which, during distillation, may be regarded as a mixture of coal substance and tar, although in different proportions. Yet it appeared possible that the tar oxidised under pressure might exert a favourable influence, as its asphalt content would supply a bituminous substance of high melting point, which, on decomposition, might induce caking; for the caking of coal requires the presence of a bitumen, which by partial decomposition assumes a higher melting point and remains fluid until converted into coke. In experiments recently made in this Institute,† directed to ascertain the amount of semi-coke required to inhibit the caking of bituminous coal, Broche found that relatively small additions would suffice, ranging from 15 per cent. upwards, according to the coal dealt with.

It would undoubtedly be most expedient to grind the semi-coke, which by nature is very friable and inflammable. It is certainly an excellent material for this purpose, and as powdered fuel application becomes more common, it would give a great impetus to the production of semi-coke and low-temperature carbonisation. For one must not fail to recognise that the production of oil by low-temperature carbonisation of coal cannot prove economical, unless a really satisfactory use is found for the 70 per cent. of residue obtained.

There is a possibility of utilising the semi-coke by adding it to strongly-intumescent coking coals. In the Saar district, for instance, it is hoped to produce a better coke by these means. Its combustion as powdered fuel, however, appears more profitable, since it can be ground with particular ease.

Matters are somewhat different with the semi-coke from brown coal

\* Brown coal tar (3.6 kg.) was oxidised for  $2\frac{1}{2}$  hours at  $200^{\circ}$ , and 35 atm., passing 400 litres of air through it.

† Unpublished.



(German "*Grude*"). This material is much appreciated for combustion on special grates on account of its peculiar capacity for incandescence. The Grude dust, moreover, can be fired in powdered-fuel burners like the dust from brown coal itself.

Apart from the ease of kindling and its combustibility, the semi-coke from bituminous coal has the further advantage of burning without producing smoke or soot. The constituents which cause smoking and sooting, essentially the ingredients of primary tar, are no longer present in the semi-coke. Differing from ordinary coke, and having retained some volatile constituents (mainly hydrogen), the semi-coke still gives a flame. Thus semi-coke may replace raw coal where heating arrangements depend on flame formation. The composition of semi-coke is compared with that of coal in Table XIII; the figures refer to dry, ash-free products, and the corresponding values for ordinary coke have been added.<sup>59</sup>

TABLE XIII

	Volatile matter. %	Coke residue. %	C. %	H. %	O. %	N. %	S. %
Orig. Lohberg coal . .	39.7	60.3	82.2	5.2	8.7	2.1	1.8
Semi-coke from Loh- berg coal . . . .	17.2-18.3	81.7-82.8	84.9	3.9	7.5	1.9	1.8
Ordinary coke . . .	2.6	97.94	96.59	0.4	O + N 1.64		1.37

The volatile matter content of semi-coke of upwards of 15 per cent. shows that degasification is not complete at a maximum temperature of 550°; a point has been reached at which the liberation of tar from the coal has ceased, but the temperature at which semi-coke passes into coke with further liberation of gas lies at 700°<sup>60</sup> or above. Hence the volatile matter in ordinary high-temperature coke is materially lower and does not exceed 2 per cent.\*

It could not be assumed that semi-coke produced at a definite temperature should have a fixed percentage of volatile matter. It was rather to be expected that on carbonising, for example, at 450°, gas would still be evolved after completion of the tar formation, as long as the semi-coke is kept at this temperature. Thus the proportion of volatile constituents left in the semi-coke would be further diminished. Anyhow, one might anticipate that the semi-coke would, after being completely freed of tar, vary in volatile matter according to the

\* At about 700° coke becomes an electric conductor, obviously by formation of carbon and gas from the still-existing carbon compounds of the semi-coke. (Fischer and Pfeiderer, *Abh. Kofte*, 1919, 4, 399).

temperature at which carbonisation had been effected. This is confirmed by more recent experiments of Broche,<sup>61</sup> which are summarised in Table XIV.

TABLE XIV  
*Volatile Matter in Semi-coke made at different Temperatures*

Coke made at  ° C.	Volatile matter.				
	After com- pletion of tar formation.  %.	After further carbonising during			
		1 hour. %.	2 hours. %.	3 hours. %.	4 hours. %.
500	7.3	6.5	6.4	5.4	5.2
480	10.1	9.9	9.2	8.3	7.5
450	12.1	11.2	10.7	10.0	8.1
430	13.3	12.1	11.3	11.0	10.2
410	13.5	12.6	12.3	11.9	11.8

Volatile matter in semi-coke from Lohberg gas flame coal is lower with higher temperature, and *vice versa*. The volatile may be 16 per cent. and more, if the carbonising temperature is kept sufficiently low. Similar observations have been made in the brown coal industry. Thus Seidenschnur<sup>62</sup> succeeded in obtaining, instead of the ordinary Grude coke, a coke of much higher volatile content which he called brown coal flame coke. This product was obtained by the cautious distillation of brown coal in a current of hot combustion gases in shaft kilns. The brown coal flame coke formed—a semi-coke with a very high percentage of volatile matter—is said to be set alight with an ordinary match, and to burn with a colourless flame right down to ashes almost free of carbon.

The gasification of semi-coke to water gas or producer gas seems to be, next to its combustion as powdered fuel, the most suitable application of this product. It has been pointed out that almost the whole of the nitrogen, and most of the sulphur, in the coal remain in the semi-coke. Economically it would therefore appear useful to use the semi-coke so that the nitrogen can be recovered in the form of ammonia, and the sulphur in the form of hydrogen sulphide.\* The gasification of the semi-coke is the best way of achieving this, for it is known that with an abundant use of steam, gasification will yield most of the coal nitrogen as ammonia. It has been found in practice that semi-coke, having lost all caking power and being highly reactive owing to its porosity, is an excellent producer fuel, and with it the throughput

\* This might be recovered as elementary sulphur with the aid of active carbon and air by the Bayer process.

of a producer is nearly doubled. It is, of course, advisable to charge the semi-coke hot as it comes from the rotary retort. The gasification of semi-coke will also render low-grade fuels, which are high in ash, available for low-temperature carbonisation, but the question in all cases will be whether suitable application can be found for the producer gas or water gas, either for heating or for power purposes.

At this stage, when speaking of the application of water gas, reference should be made to interesting and promising experiments on the preparation of liquid fuels from water gas. They concern the conversion, by catalytic processes under pressure, of water gas into liquid fuels, and will be described in a separate chapter (Synthol process).

#### (n) THE HEAT BALANCE OF LOW-TEMPERATURE CARBONISATION

The heat balance of low-temperature carbonisation and of the thermal decomposition of coal in general has formed the subject of several investigations.<sup>63</sup> According to Strache and Grau,<sup>64</sup> the gross heat of carbonisation is "the quantity of heat, referred to liquid water and liquid tar at 0°, which is either absorbed or liberated by the chemical process of gas-making (heat of decomposition), plus the caloric energy necessary for overcoming external work in the formation of gas. The net heat of carbonisation is that referred to water and tar, not in the liquid, but in the vapour state. This value is obtained by subtracting the heats of vaporisation of water and tar from the gross heat of carbonisation." The experiments performed with coal, brown coal, wood and cellulose indicated a certain relation between the sign of the gross value and the oxygen percentage of the material. Table XV gives the values and means for the gross heat of carbonisation. In the case of bituminous coal the figures are mostly negative (endothermic); its carbonisation requires therefore a continual supply of external heat.

Brown coal and lignite, on the other hand, show a positive heat of carbonisation (exothermic) which is largest in the case of wood, and it has long been known in charcoal burning that carbonisation, once started, progresses spontaneously with considerable liberation of heat.

TABLE XV

(a) Bituminous Coal I:	- 16; - 15; - 15; + 19; - 13; + 30; - 57; - 2; - 4; Mean = - 8 Calories.
(b) Bituminous Coal II:	- 26; + 12; - 10; Mean = - 8 Calories.
(c) Brown Coal I:	+ 52; + 60; + 35; Mean = + 49 Calories.
(d) Brown Coal II:	+ 60; + 35; + 45; + 54; + 64; + 98; + 25; + 80; + 49; + 54; Mean = + 54 Calories.
(e) Lignite:	+ 103; + 109; + 112; Mean = + 108 Calories.
(f) Wood:	+ 118; + 366; + 178; + 165; + 323; + 276; + 190; + 232; Mean = + 231 Calories.

The upper curve of Fig. 9 represents graphically the relation between the oxygen percentage of an ash-free, dry fuel and its gross heat of carbonisation. With an oxygen content above 12 per cent. the value is positive; with lower oxygen it is negative.

In practice, however, not the gross but the net value is in question, since the distillation products are liberated, not as liquids, but as vapours. The latent heat of the condensate must therefore be deducted from the gross heat of carbonisation, to arrive at the net values. By this calculation the higher grade of brown coal is found to approach bituminous coals, *i.e.*, fuels subject to endothermic decomposition.

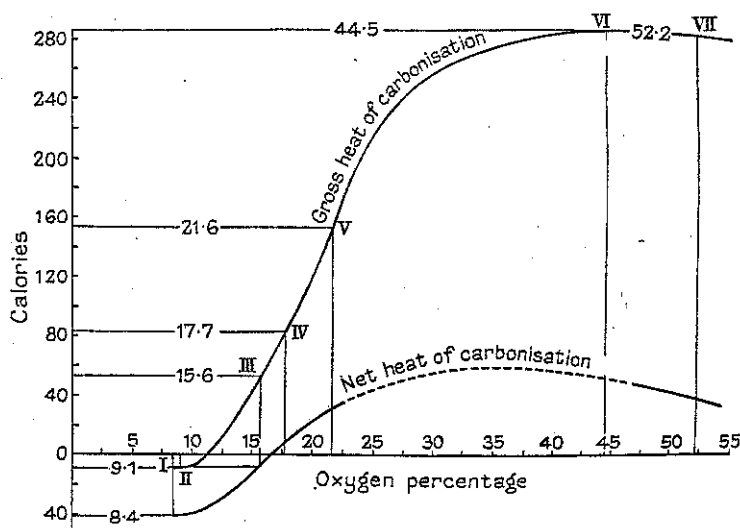


FIG. 9.

The lower curve of Fig. 9 represents the course of the net heats of carbonisation. Here the demarcation between an exothermic and endothermic heat balance is shown by an oxygen content of the fuel of 17 per cent.

Strache and Frohn<sup>65</sup> summarise their conclusions as follows: Bituminous coal and good brown coal require for their carbonisation a sustained supply of heat, whilst low-grade brown coal, wood and cellulose liberate heat. With increasing oxygen percentage, therefore, the calorific value and the heat required for carbonisation diminish.

These statements, of course, hold only for completely dry fuel preheated to the temperature at which carbonisation begins. The difference becomes noticeable only at that stage when materials relatively poor in oxygen require a continued supply of heat for their complete degasification; whilst with the decomposition of materials richer in oxygen, degasification proceeds spontaneously with more or less liberation of heat. Starting, however, with fuel

of a natural moisture content, the position is altered inasmuch as external heat must be supplied both for drying and thermal decomposition, and the differences in the total heats required will then not be those between the net heats of carbonisation. Let us assume a poor brown coal containing 50 per cent. moisture (quite a common value), and let us further assume the coal to be free of ash. The heat of carbonisation liberated by 2 kg. of this coal corresponding to, say, 1 kg. of ash-free dry fuel may be 50 Calories; but about 600 Calories would be required for vaporising the 1 kg. of water contained in 2 kg. of raw coal. Hence, in practice, the endothermic carbonisation of bituminous coal, which contains little moisture, required less heat than the intrinsically exothermic carbonisation of brown coal, if the latter is used in its raw state containing up to 50 per cent. of moisture. Since carbonisation is always preceded by drying, external heat must needs be supplied when fuels in their natural moist state are carbonised.

(o) *The Development of Commercial Primary Tar Production.*

It should at once be pointed out that primary tar production has by no means assumed final shape, as high-temperature coking has done. It is still in a state of development and of the various systems known, those which seem most likely to meet all requirements have to be perfected. The first aim in distillation processes in which gasification or combustion of the semi-coke plays no part should be to obtain a tar free from dust and water. It might also be possible to effect, with a well-conducted distillation process, a fractional condensation of the oils, which would admit of withdrawing pitch, viscous oils, fuel oils and benzine at suitable stages. With a continuous process, this should be far easier than in coke-ovens, in view of the smaller make of gas in low-temperature carbonisation relative to the quantity of oil obtained. The coking process is intermittent, and the production of gas and tar is therefore not uniform, as is necessary for a fractional condensation of the tar constituents. Fractional condensation is rendered much more difficult when the tar vapours are diluted with many times their volume of non-condensable gas. If, therefore, the adoption of fractional condensation has been a qualified success only in a few coke-oven plants (Feld process), it may be more promising in low-temperature carbonisation. In the coking process, some 250 cb.m. of gas are made per ton of coal carbonised, together with about 3 per cent. of tar, or, say, 30 kg. per ton. Before being condensed the 30 kg. of tar vapours will therefore be diluted with 250 cb.m. of gas. In the low-temperature coking of gas coal, on the other hand, a ton of coal will yield 50 cb.m. of gas and 10 per cent., or 100 kg., of tar. In this case 100 kg. of tar vapours will be diluted with 50 cb.m. of gas before entering the condenser. The concentration of tar vapours in the gas is therefore more than fifteen times as large, and the

conditions for fractional condensation will be correspondingly more favourable. As the working cost of the fractional condensation is no higher than those for the condensation of the total tar as now practised, it is obvious that a plant for the production of low-temperature tar will be more economical, if it is able to supply four finished products instead of an emulsion of tar, dust and water, which must subsequently be worked up at additional costs, as is still frequently the case.

Many critics of primary tar production have rightly emphasised that the semi-coke amounting to 70 per cent. of the coal is not obtained in a readily utilisable form. This objection is met easiest by carbonising only such coals as yield a firm semi-coke. Such coals are known and many others may be found. The possibility of compressing the semi-coke during its production has already been discussed, as well as its utilisation as powdered fuel (p. 50). In general, however, it will be obtained in a form unsuitable for direct use. It must be either briquetted, or ground for powdered fuel. Semi-coke would appear to be directly applicable only as producer fuel, where it even offers advantages. In Chapter IV of this book it will be shown that a combination of primary tar production with the Synthol process via water gas from semi-coke constitutes an ideal method of oil production from coal.

When speaking of primary tar production as being still in the stage of development, the working-up of the oils obtained must be considered. For what use would it be to produce various kinds of crude oils if they have to be freed, by costly methods, of constituents objectionable for certain purposes and if no use can be found for these? For example, the fuel oils from the low-temperature carbonisation of gas coal, the richest in tar yield, contain not less than 50 per cent. of phenols. That these phenols can be removed by inexpensive processes and that they can be converted into useful products I shall show in two further chapters which will deal with the extraction of phenols by superheated water and with the reduction of phenols to benzene and toluene by the aid of hydrogen. I shall also point out that the hydrogen required for this purpose can be prepared from water gas or producer gas by means of a special process based on diffusion against steam. I am firmly convinced that primary tar production will only be placed on a sound basis when the different requirements mentioned are satisfied.

In reviewing the development of commercial primary tar production, I shall first indicate the various methods opened up by scientific experience and technical possibilities, and I shall then describe plants corresponding to each type. I shall, however, refrain from mentioning all the innumerable patents, and from reproducing drawings in as far as they offer no particular interest.

(1) *Distillation Apparatus with External Heating.*—Distillation apparatus in which the semi-coke is not further worked up may be divided into two

classes depending upon external heating, where the heat is transmitted from outside through a wall, and internal heating where carbonisation is directly effected by hot gases passing through the charge.

The apparatus for external heating may be further divided into stationary and rotary furnaces.

The stationary furnaces may be shaft furnaces, horizontal retorts or tunnel kilns.

*Vertical Retorts.*—If the production of low boiling benzine and gas is aimed at, the coal is best distilled by applying external heating. The relatively low temperature of  $400^{\circ}$  to  $500^{\circ}$  required for this purpose admits of the use of retorts of steel or cast-iron, which are preferable to refractory material on account of their impermeability to gas and greater thermal conductivity. Stationary retorts offer the advantage over rotary furnaces that they do not require a power drive. The rate of distillation depends upon the thermal conductivity of the walls and the thickness of the layer of coal. In view of the low thermal conductivity of coal and the resulting semi-coke, that layer should be as thin as possible, so as to keep the carbonising period at the low temperature gradient reasonably short and provide for an economical throughput of the retort. An attempt to raise the throughput by more intense heating of the retort wall would lead to superheating the tar vapours, diminish the tar yield and lower the quality, *i.e.*, its hydrogen percentage. In other words, a product would result which in quantity and character would approximate to coke-oven tar. This is a defect of all processes which profess to produce primary tar, but claim at the same time to realise very high yields of ammonia. These become possible only at temperatures from  $600^{\circ}$  to  $800^{\circ}$ , whilst in the normal low-temperature tar production most of the nitrogen remains in the semi-coke. It may be subsequently recovered as ammonia by gasification of the semi-coke much more completely than would be possible by applying higher carbonising temperatures.

To avoid hanging-up of the charge of highly caking or swelling coals and difficulties in discharging, the vertical retorts are given a suitable taper.

The English "Coalite" process was probably the first to be commercially applied for the low-temperature carbonisation of coal.<sup>66</sup>

Fig. 10 gives two longitudinal sections and a cross-section of the retort.

The above applies to this process in particular. It should be mentioned, however, that the Coalite process was not designed for the production of oil, but essentially for the production of a smokeless fuel.

The process of the Premier Tarless Fuels, Ltd., is based on similar principles and aims at the same object (Fig. 11). As in the Coalite process, cast-iron vertical retorts are used, but they are formed into annular carbonising chambers. Experiments were made as early as 1900 on the Coalite process, and working on a large scale started in 1906. Later the use of cast-iron

retorts proved unsatisfactory. Under the influence of heat the cast-iron began to "grow," the connections developed leaks, and the retorts cracked, became porous and had to be replaced at short intervals. Although the retorts were tapered, the coke could only be discharged with the aid of rods and other tools to the detriment of its quality and size. A tendency to spontaneous ignition of the semi-coke also caused difficulties. Heavy quenching proved necessary, which made it water-logged and increased its brittleness. For these reasons fire-clay retorts were adopted, and quenching of the semi-coke with water was abandoned and replaced by cooling in water-jacketed

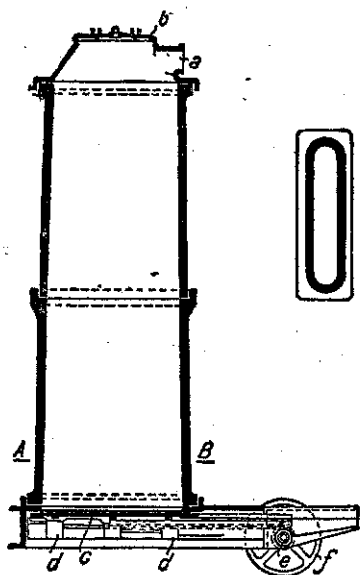


FIG. 10.

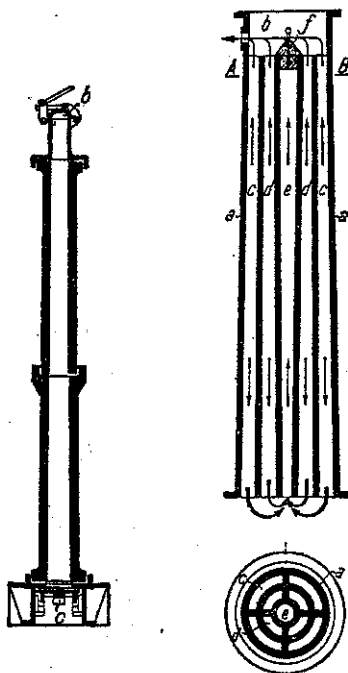


FIG. 11.

chambers, in the absence of air. Details of these modifications have been described in the literature.<sup>67</sup>

Another system in which vertical retorts are employed is that of Greene-Laucks, at Denver (Colorado).<sup>68</sup> The retorts are of cast-iron, 5.5 metres high and 0.4 metre diameter. As Fig. 12 shows, an external spiral rib is cast on the retort to serve in conjunction with the setting as a flue. An internal screw conveyor is intended to keep the coal in motion, and its hollow shaft is perforated to allow the distillation gases to escape. Apparently the plant is of an entirely experimental character.

The large-scale test plant, consisting of horizontal steel retorts, at H.M.



Fuel Research Station, Greenwich,<sup>69</sup> was designed by the late Sir George Beilby, mainly for the purpose of correlating laboratory and works results. It was

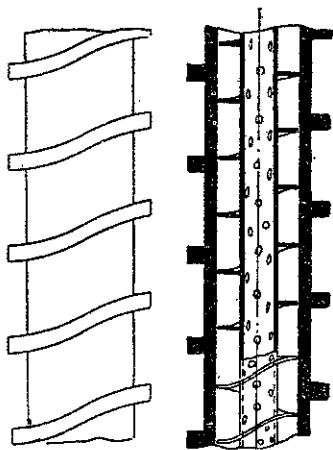


FIG. 12.

intended for experiments in which tons and hundredweights could be dealt with under standard conditions which could be reproduced at will on an industrial scale.

Whilst the processes mentioned so far concern the production of primary tar and semi-coke from bituminous coal, retorts for the treatment of brown coal and of oil shales have long been used. These materials present no difficulty by caking or swelling, and if they are very rich in tar, the properties of the solid residue are of no consequence for the economy of the system as in the case of coal. The plants were not designed for producing primary tar. There was no interest in undecomposed bitumen, and the object was the production of well-crystallised

paraffin wax, gas oil and fuel oil. Even the production of benzine from the carbonising gas was not a decisive factor in these older processes. Three of the most important types used may be mentioned.

In the Central German carbonising industry, the Rolle furnace has been used for many years. It is intended for the use of raw brown coal, which, air-dried by suitable storage, admits of continuous working. The height of the retorts reaches 10 metres.

The retort is built of firebricks and is surrounded by flues. The coal slides down between the walls of the retort and an inner cylindrical body, built up Venetian-blind fashion, of a series of bells resting upon one another, through which the gases and vapours find an outlet. Large numbers of such retorts have been in operation for many years in Central Germany.

Another retort system is in use at Gewerkschaft Messel, near Darmstadt, where shale in lump form is carbonised. The Rolle furnace, which is designed for powdered material, would be less suitable in this case. The large size of the Messel shale permits of the application of superheated

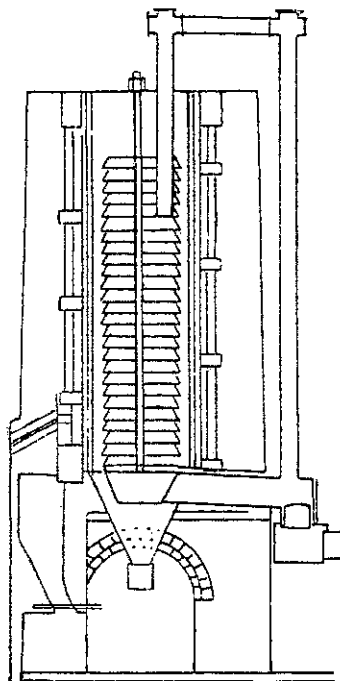


FIG. 13.

steam to facilitate carbonisation. Fig. 14 explains the principle of this retort; further details will be found in Scheithauer, "Die Gewinnung der Schwelteere," 2nd edition, p. 50.

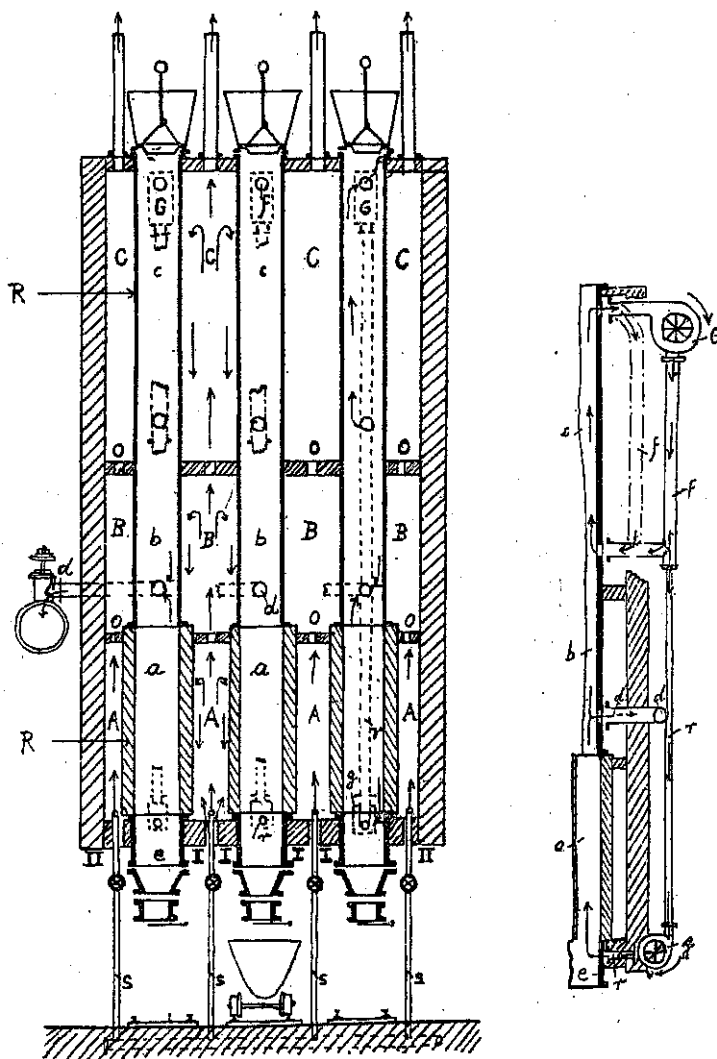


FIG. 14.

The type of furnace illustrated in Fig. 15 is representative of the Scottish oil-shale retort. It is due to Bryson, and was erected at Pumpherston. Four retorts are built into one setting, their upper portion being made of cast iron, the lower portion of firebrick. The retorts are 9 metres high, charged from above, and discharged below through a common hopper.

Although the retorts used at Messel and in Scotland are not really intended for bituminous coal, it is useful to refer to them since the experiences gained with them in decades of successful working is of value in the production of oil from coal.

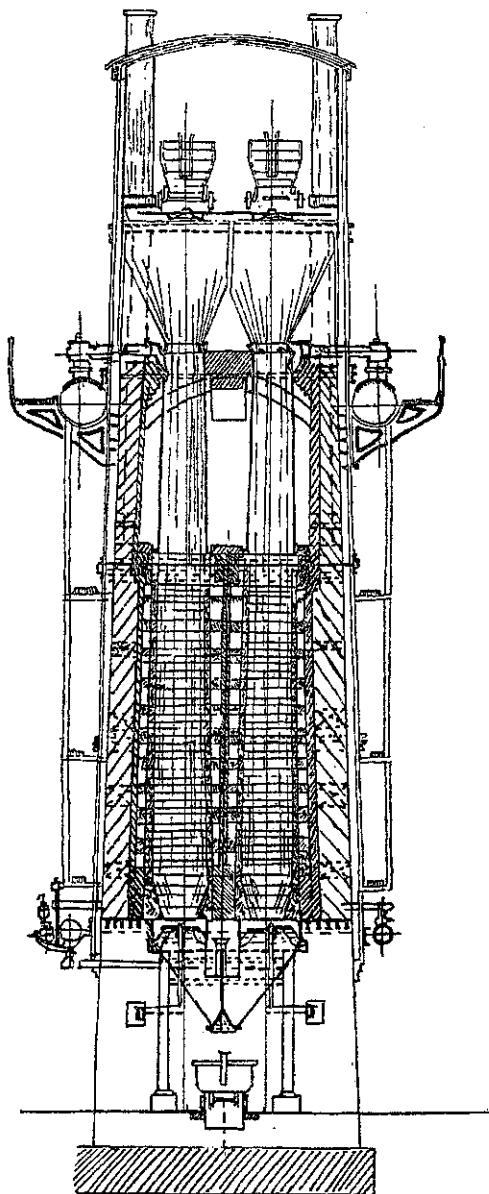


FIG. 15.

at Clinchfield, started up in 1920, is one of the few which may claim to have assumed large industrial dimensions. Horizontal retorts are used which are

*Horizontal Retorts.*—The process of Del Monte-Everett (Fig. 16) is continuous. The slightly inclined tubular retort is made of cast steel. The coal is introduced at the lower end and is carried through the tube by a worm conveyor. At the upper end the semi-coke is cooled in the absence of air.

The retort is lagged with a refractory lining and is built with several others into a brickwork setting. The gas leaves at the lower end of the retort; after condensing oil and water, the gas is blown again into the upper end of the retort after having passed through a superheater. The distillation is therefore effected partly by external heating and is accelerated by a circulating current of superheated gas. The surplus gas formed in the process is taken out of circulation and utilised for the external heating of the retort. An experimental plant of this kind was in use at Chiswick, London. The plant was stated to yield exceptionally high percentages of oil, due to the circulation of gas and the consequently rapid removal of the oil from the retort.

The Carbocoal process (Figs. 17 and 18), which was developed in America from an experimental installation at Irvington into a large plant

outside heated, somewhat on the lines of the bottom-heated Otto coke-oven. The retorts are built of firebrick and have a cross-section shaped like an inverted heart; they are 6 metres long, 2 metres wide and 1.5 metres high. Blades bolted to two shafts serve as mixing and conveying worms. The description of the plant leaves the impression that it has been built with great care and unusual technical resources. The Carbocoal process has the following peculiar features: The coal is converted into semi-coke while travelling through the horizontal retorts. The gaseous products are withdrawn at the

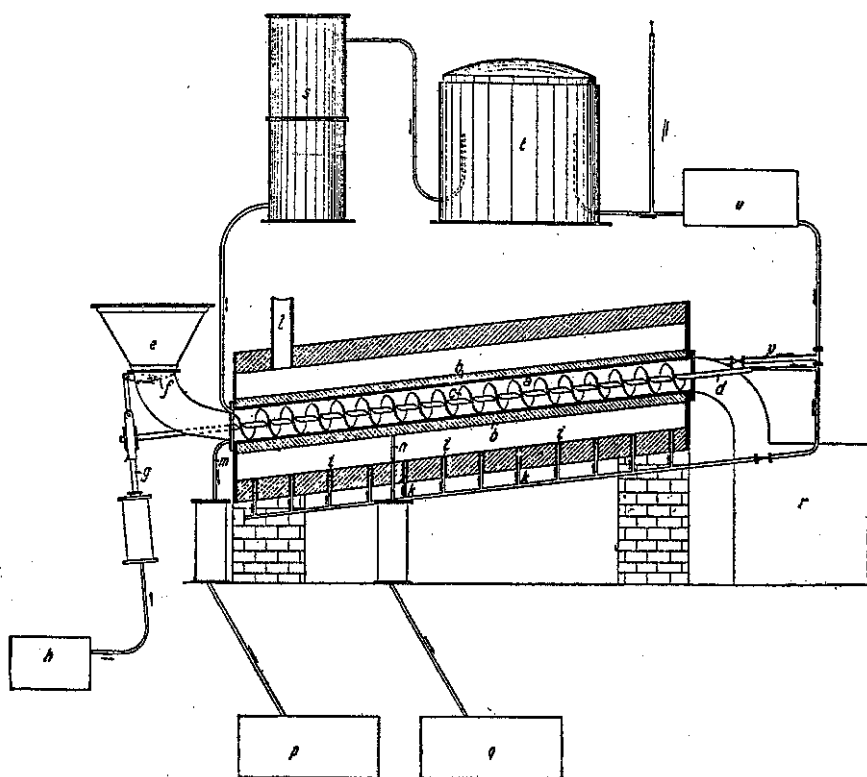
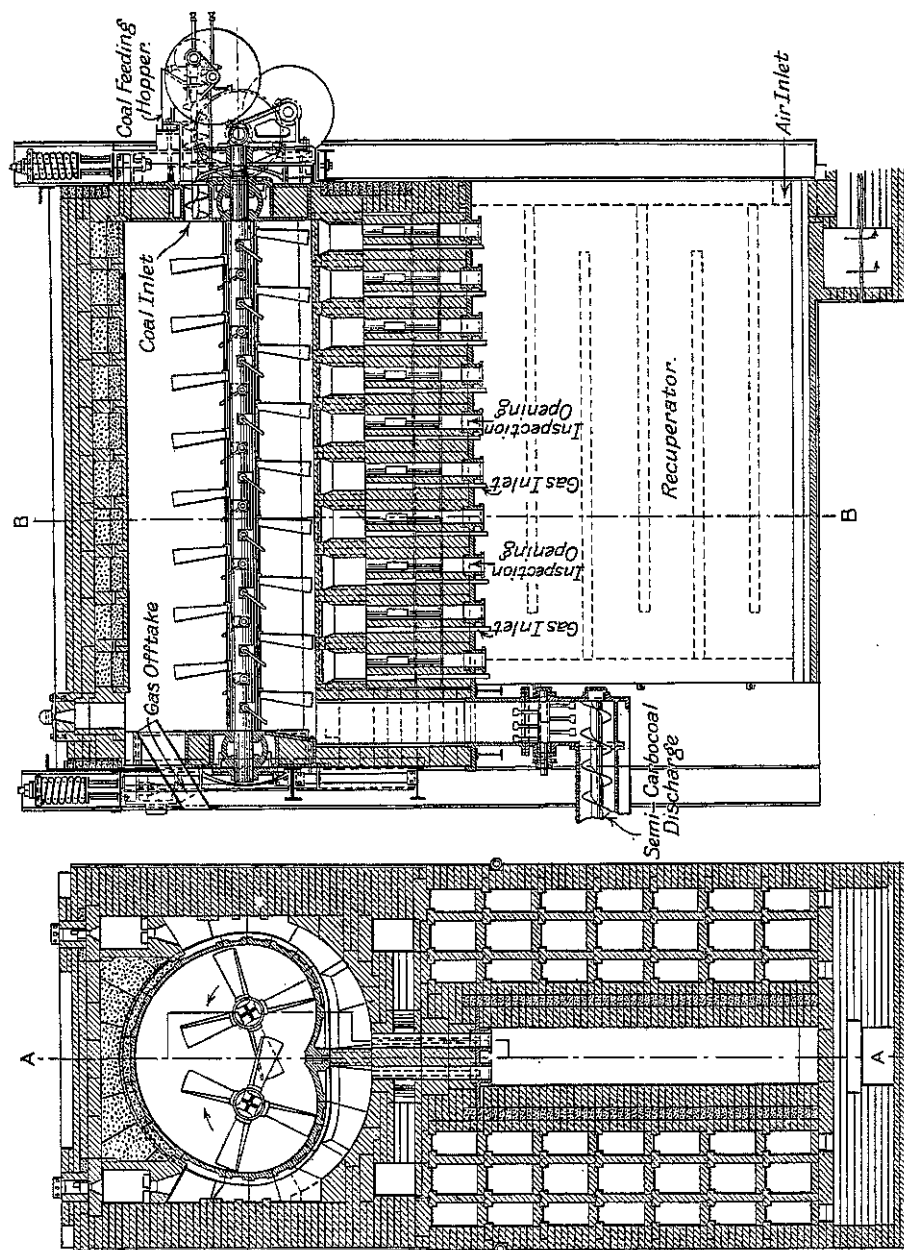


FIG. 16.

end opposite to the charging side, whilst the semi-coke drops through a vertical shaft to be ground in hammer mills and pressed into ovoid briquettes with an admixture of from 10 to 12 per cent. of liquid pitch. The briquettes cannot be utilised as smokeless fuel on account of their pitch content. They are, therefore, subsequently carbonised in high-temperature secondary retorts (Fig. 19) yielding smokeless fuel and a tar similar to coke-oven tar.

It has been repeatedly emphasised that a suitable application of semi-coke is an essential requisite for the economy of primary tar production. In the case of the Carbocoal process, there is no doubt that it can yield a primary

tar, nor will it be questioned that the final product is a useful solid fuel of convenient shape. The methods by which this end is attained give rise to



Section A.A.  
FIG. 18.

Section B.B.  
FIG. 17.

grave objections on economic grounds. The pitch required for briquetting the semi-coke cannot be obtained from the corresponding weight of coal in

sufficient quantity. It must be assumed that the products of the high-temperature retort are re-introduced again and again into the pitch cycle, or else pitch must be bought from outside. In any event briquetting and repeated carbonisation are very costly, and cast considerable doubt on the commercial possibilities of the process. Early objections by various experts were confirmed by the extensive reports of Curtis and Chapman.<sup>70</sup> They show that many difficulties had to be overcome, and that no fewer than twenty-five different retorts were constructed, most of which were actually

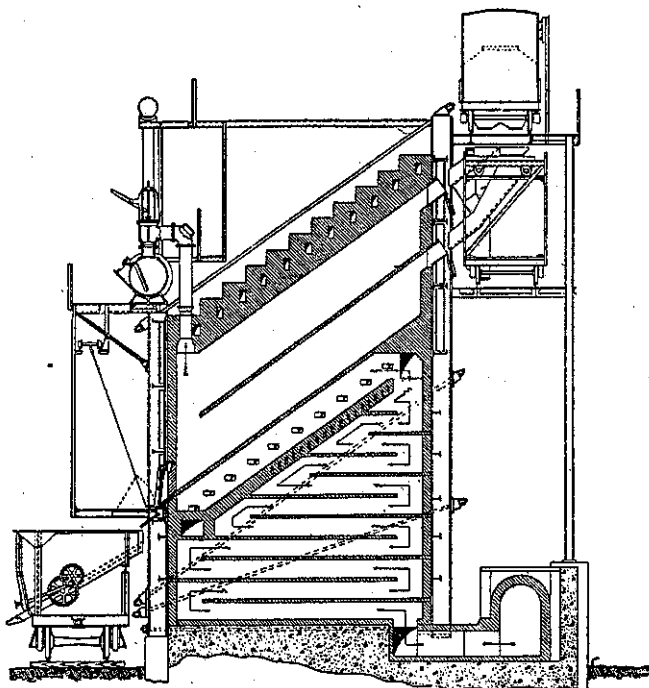


FIG. 19.

tried. The greatest difficulties caused by the conversion of the semi-coke into a smokeless fuel and its economic failure led eventually to the closing-down of the plant early in 1922. One is probably not mistaken in assuming that the plant, which was subventioned by the American Government, chiefly aimed at the production of a smokeless fuel, and that the production of oil was considered of secondary importance in America, where oil abounds. \* If one is at all justified to speak of the "failure" of the plant, it would chiefly relate to the production of a firm smokeless fuel, an object which is paramount in other countries where low-temperature carbonisation has to be conducted for the sake of the oil, especially if it is considered that there are other useful applications for semi-coke.

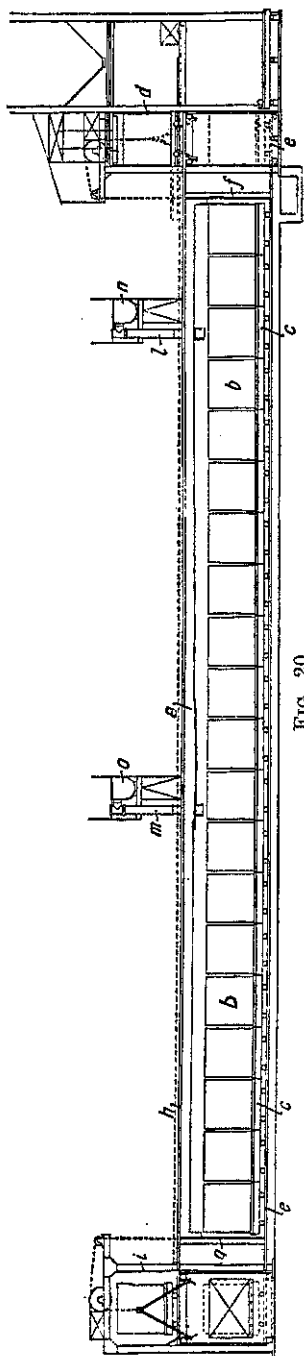


FIG. 20.

*Tunnel Kilns.*—It has also been proposed to effect continuous low-temperature carbonisation by means of tunnel kilns similar to those used in the ceramic industry. One essential advantage of the tunnel kiln is, that in distinction from the rotary retort, it avoids not only the disintegration and pulverisation of coal and hence the very unpleasant formation of dust, but also admits of the utilisation of small and generally poorer grades of coal. By stamping or pressing, such fuels can be shaped into briquettes of suitable size and be carried through the kiln on small trucks. Tunnel kilns occupy more ground space than rotary retorts, but have the advantage of being able to deal with smalls without creating a dust nuisance, and this may weigh heavily in their favour against rotary retorts under certain local conditions.

The Patent literature affords several proposals for the use of tunnel kilns for low-temperature carbonisation. As far as I am aware, the only large tunnel kiln actually built is that of the Westdeutsche Industriebau A.-G., at the Konstantin der Grosse Colliery at Steele-Ruhr. Figs. 20 and 21 give longitudinal and transverse sections through the kiln. The kiln is comparatively narrow and high, resembling a coke-oven in cross section and in the mode of heating. The bogey of the trucks is protected from the heat by a refractory slab on which the briquettes to be carbonised are stacked checker-work fashion. The trucks are pushed

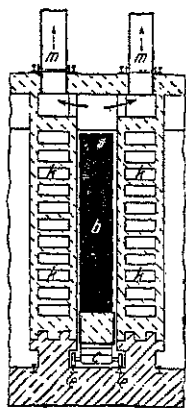


FIG. 21.

into the tunnel, one at a time through a lock, so that the train in the tunnel advances by one truck-length, whilst at the other end one truck leaves the discharge lock. The tunnel is heated through flues provided in the setting, the highest temperature being in the middle portion. The hot combustion gases pass along the horizontal flues towards the truck inlet and

into the chimney; they are thus moved in the opposite direction to the truck. In the other half of the tunnel, air is admitted through the flues from the discharge end of the coke and is directed towards the burners of the carbonising zone. The coke blocks on the trucks are cooled whilst travelling through this half of the tunnel, and transmit, through the brickwork, part of their heat to the air, which thus becomes more and more preheated as it approaches the burners.

The products of distillation are taken by numerous pipes to a collecting main. The tar is said to be quite free of dust.

Whether an entirely unchanged primary tar can be obtained in this tunnel kiln will depend upon the mode of operation. The strong exhauster action

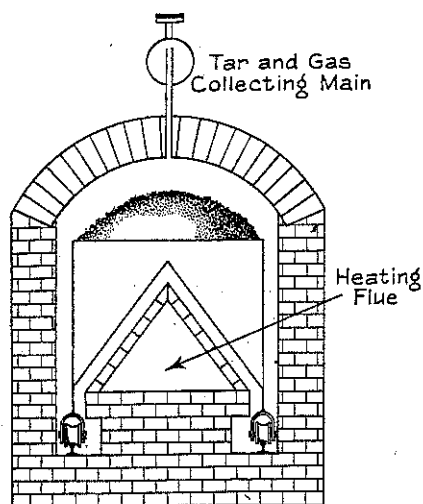


FIG. 22.

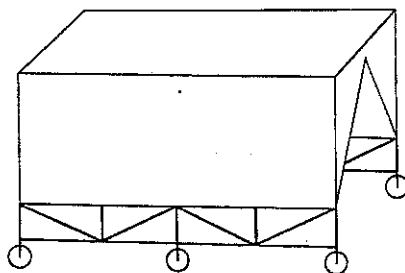


FIG. 23.

required probably keeps the tar vapours issuing from the briquettes from prolonged contact with the hot walls and thus prevents decomposition.

The "Central Channel Kiln" is a tunnel kiln designed to avoid such contact, and especially intended for primary tar production. The wagons run astride a flue which is triangular in section as shown in Figs. 22 and 23. The coal used may be smalls, lumps or briquettes, and the wagons will accordingly be built of sheet metal or of lattice work. The heat is transmitted to the wagons practically from inside. The products of distillation escape outward, and are withdrawn from the top of the outer arches. Longer carbonising periods are required with this arrangement than with tunnel kilns of the coke-oven type, but the products of distillation are less liable to secondary decomposition. In this type of truck, the semi-coke might be



compressed during its formation by means of a heavy perforated plate put on the coal.

On coming out of the tunnel, the wagons are quickly discharged by lifting their side walls. The central flue is heated in its middle portion only. Here again the products of combustion pass in counter-flow to the wagons towards the smoke stack, remaining completely separated by the flue wall, from the distillation chamber in which the wagons are running. The outer walls of the tunnel need not be heated, but require good heat insulation.

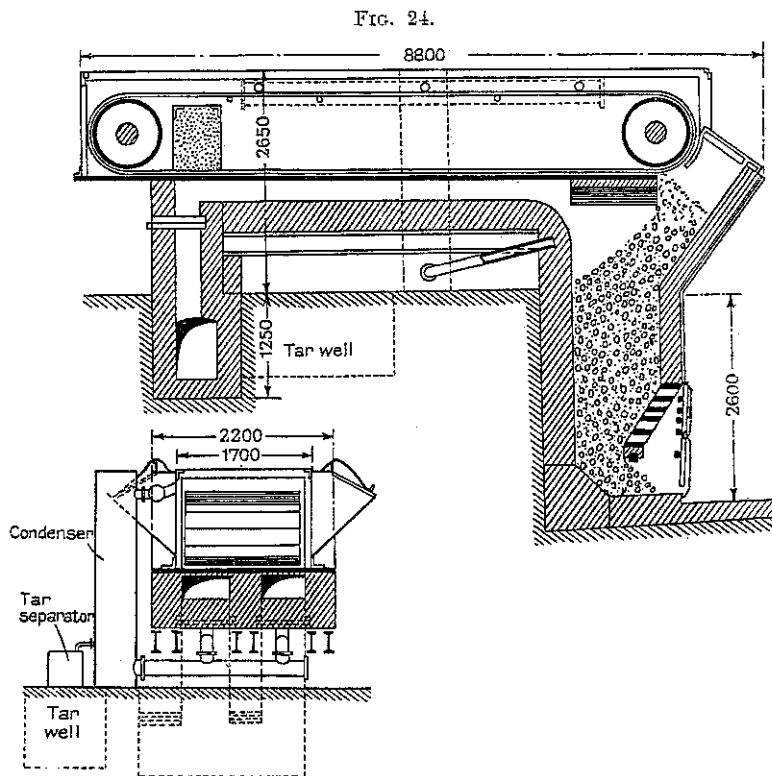


FIG. 25.

The principle of the Carthaus System will be understood from the diagram of Figs. 24 and 25. The fuel is spread in a thin layer on a belt conveyor which is drawn along the top of the cast-iron plate. This plate forms the crown of a heating flue and transmits the heat quickly to the flue. The belt conveyor runs over two pulleys, receives the fuel at one end and throws off the residue at the other end. The distillation products are withdrawn through ports provided in the casing which surround the belt conveyor. The throughput of this plant is stated to reach 18 tons of shale per 24 hours. I am

not aware of any practical tests of the Carthaus System, but it represents a type of its own which might be modified into a tunnel kiln.

*Rotary Retorts.*—Rotary retorts have found special favour in Germany, their prototype being Fischer and Gluud's rotating drum laboratory apparatus. Whilst the drum was devised for charges of 10 to 20 kg. of coal only and had therefore to be operated intermittently, the large-scale rotary retorts were designed for continuous working. The first rotary retorts of really large dimensions were designed by Dr. Roser<sup>71</sup> of Messrs. Thyssen & Co., Mülheim-Ruhr, a few years ago. At present there is a plant for 100 tons throughput per day at Thyssen & Co.'s works, two units at the Graf Bismarck Colliery, and one other installation at the Hamburg Gasworks. The Thyssen rotary retorts are of surprising simplicity and capacity. The iron drums are built in one piece of 24 metres length and 2.5 metres diameter.

Fig. 26 illustrates a Thyssen rotary retort heated by producer gas and combined with a semi-coke gas generator; Fig. 27 is a view of the two retorts at Graf Bismarck Colliery.

The coal fed into the rotating tube at one end is carried in two hours through the 24-metre length of tube, by means of helical screw lifters riveted to the drum, and drops out at the other end in the form of a semi-coke. The iron drum runs in a chamber which is fired with producer gas, and lagged by strong brick walls against heat losses. The distillation gases leave the drum together with the tar vapours at the same end as the semi-coke. It is questionable whether this is the most suitable arrangement. I shall revert to this point in a special section on "The Influence of Retort Design." According to Messrs. Thyssen, the liquid carbonising products equal in quantity and quality those obtained by careful laboratory working with the Fischer rotating drum. The only difficulty with which the Thyssen plant has to contend is the formation of dust.

In most low-temperature retorts the escaping gases and tar vapours carry with them coal dust or, more correctly, semi-coke dust. This dust trouble is particularly pronounced in large rotary retorts, because the friable semi-coke is kept in rolling and tumbling motion, and the dust, once produced, is continuously being stirred up.

As the presence of dust in the tar interferes with the separation of the water and lowers the value generally, it is necessary to remove it before the tar is condensed. In our laboratory apparatus we used a dust separator fixed in the drum,\* so as to deposit the dust at the temperature of the furnace, i.e., free from tar. The high boiling tar fractions were then condensed at 150° and, therefore, free from water.

The lower boiling fractions and the liquor were subsequently condensed by cooling with water, the liquor being separated from the oil in the ordinary way. It is therefore not difficult to produce a tar free of dust and water,

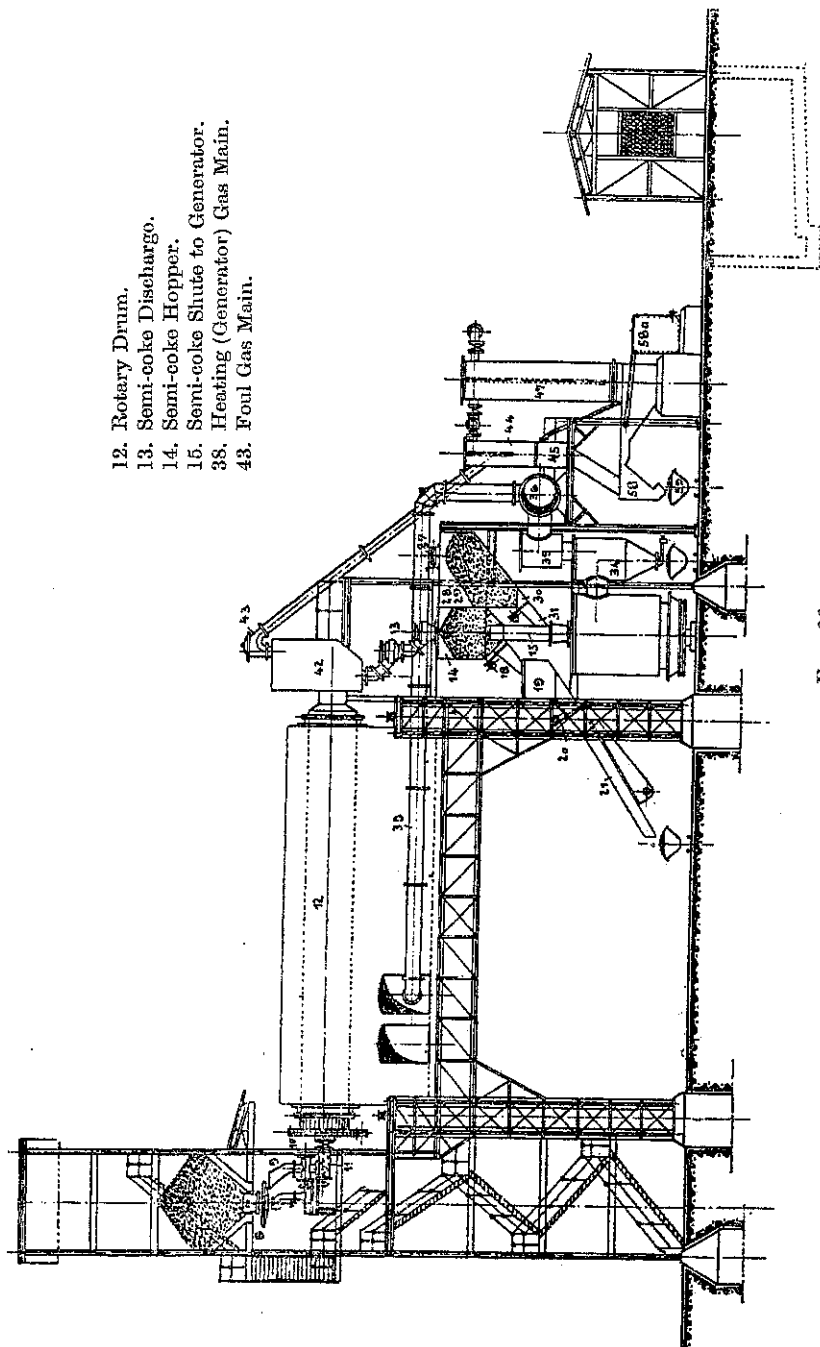


FIG. 20.

if the dust is eliminated, say, at 400° in a heated separator, the high boiling tar at 150°, and the lighter oils and liquor at ordinary temperature. The problem has also been solved in connection with works plant; heated dust eliminators are arranged as separate units, in preference to building them into the retort drums.

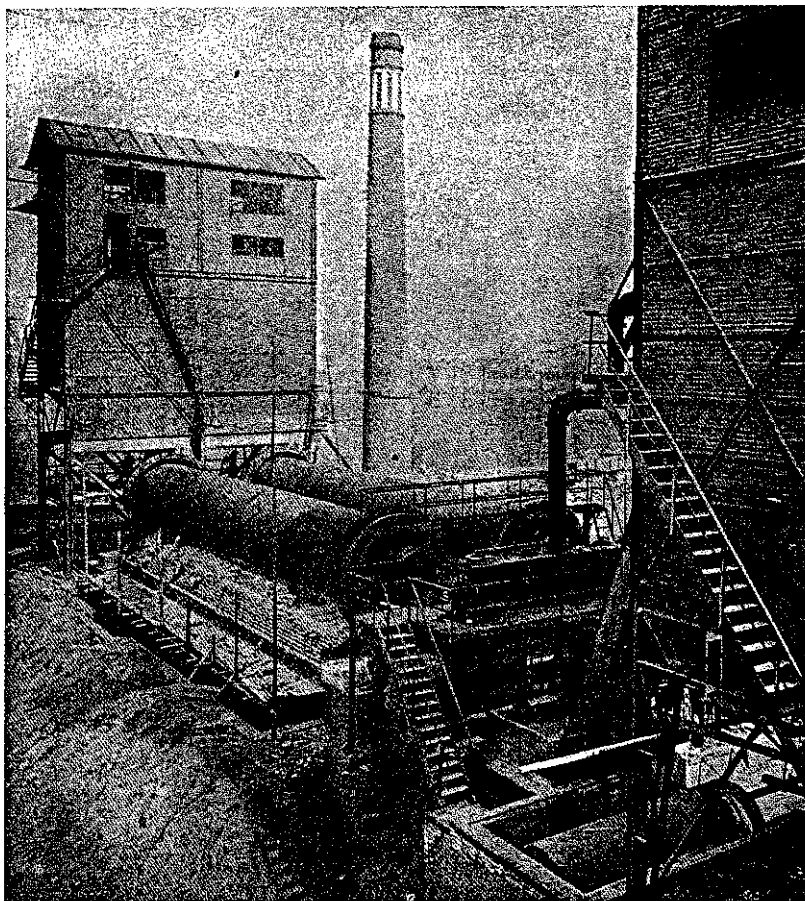


FIG. 27.

The Thyssen installations are usually provided with benzene recovery plants in which the benzene is washed out of the gas by means of oil. This benzene is a valuable motor spirit.

Fellner and Ziegler of Frankfort-on-Main have erected a rotary retort plant for the Gelsenkirchener Bergwerks-A.-G. This plant has been described in detail by Thau.<sup>72</sup> Figs. 28 to 31 show the essential features of this system.

Whilst the Thyssen rotary retort is mounted horizontally, that of Fellner

and Ziegler is slightly inclined. They can therefore dispense with the helical screw, but they run the risk that the whole charge may slide down, as occasionally happens in rotary cement kilns. It is questionable whether this risk need be considered in the case of caking coal. The plant seems to be very well designed and carefully executed. The drum is made of riveted mild steel plates, 18 mm. thick; it has a length of 20 metres, an internal diameter of 2.5 metres, and an inclination of 5 per cent., so that one end lies 1 metre lower than the other. The retort is heated with blast furnace gas which is effective enough in spite of its low calorific value, and has the added advantage of giving a long and uniform

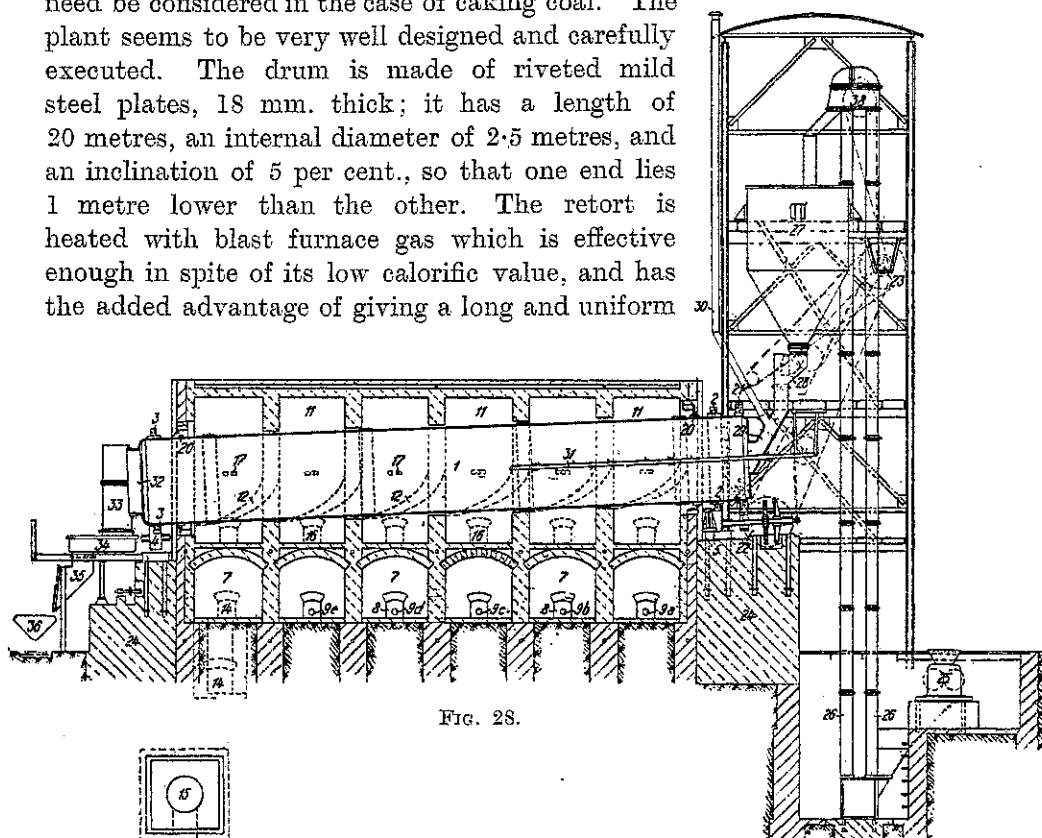


FIG. 28.

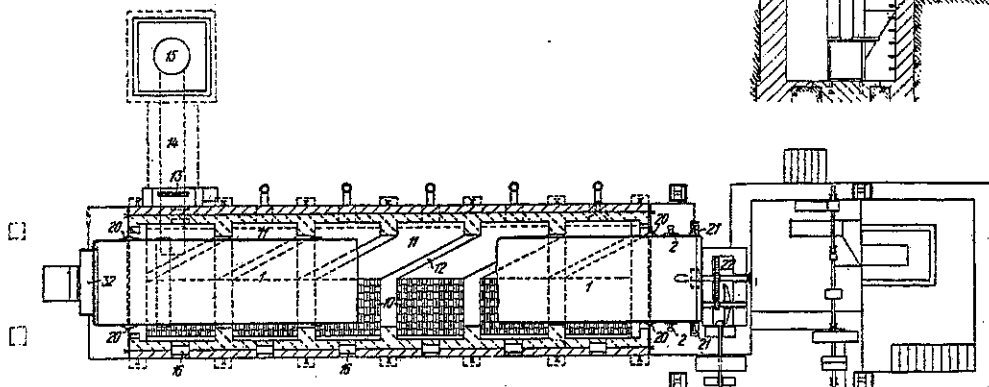


FIG. 29.

flame. The carbonising gas leaves the drum at the same end at which the coke is discharged, and after passing the dust separator, enters the condenser for the separation of the tar and water. The tar contains relatively much water and requires special treatment. This plant does not yet comply with

the demand for a tar free of water and of dust. The gas, after removal of the tar, is stripped of its benzine in a special plant after the design of a benzol factory.

The Kohlenscheidungs-Gesellschaft, of Essen, is erecting on one of the Stinnes collieries an iron rotary retort which differs from the two types just described in that it consists of two concentric tubes. The coal travels first along the inner tube from one end to the other, being at the same time dried and preheated; it then drops into the outer tube, and travels back the whole distance. The advantage claimed is a better utilisation of heat, owing to the compactness and greater stability of the whole setting. The mode of firing is said to be novel. Whilst with other types the low temperature of the heating gas required is obtained by admitting a large excess of air, the combustion is in this case effected with the least possible excess of air. After this combustion, which secures the highest degree of efficiency, the temperature of the fire gases is reduced by mixing them with waste flue gases which are continually circulated through the flues. Apart from high thermal efficiency, the system offers the advantage that the temperature may very quickly be adjusted to any desired degree, and that the high gas velocities attainable ensure a superior heat transmission to the carbonising drum.

The firm of Méguin A.-G.<sup>73</sup> has erected an experimental vertical rotary retort at Butzbach, Hessen. In this furnace the coal is intended to be compressed during the carbonisation by centrifugal force; the tar is said to be free of dust.

Attention has recently been paid outside Germany to externally-heated rotating retorts on a principle closely related to that of the Kohlenscheidungs-G.m.b.H.

Goodwin<sup>74</sup> gives the following particulars of the "Fusion" retort: The retort (Figs. 32 and 33) consists of two concentric tubes, *a* and *b*. The coal is fed into the inner tube, which it traverses from one end to the other, and then drops into the outer tube, in which it is carried back. In the inner tube is placed a loose "star" or "cross" breaker, which in rotating is carried up and falls back so that one edge of the stars or crosses

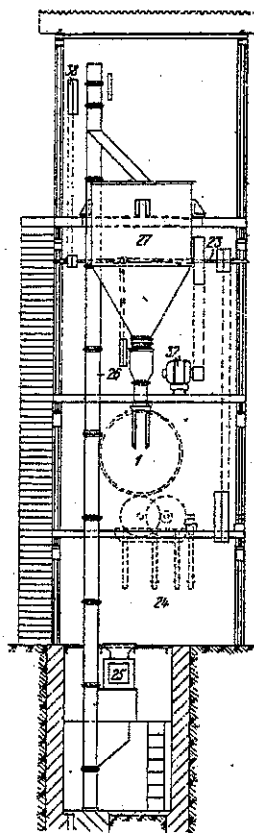


FIG. 30.

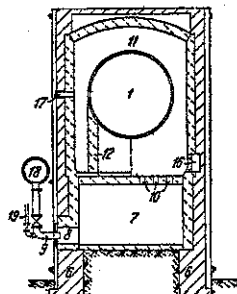


FIG. 31.

gives a chipping or hammer effect to the material being treated. The products of the distillation are taken off at *o*. The retort has the advantage that it needs a gland at one end only; the other end, at which the coal drops from the one tube into the other, may be sealed.

*Retorts with Inner Lining.*—Thomas <sup>75</sup> has designed a rotary retort for continuous operation (Figs. 34 and 35). It consists of a cylinder of iron, up to 30 metres in length. It is lined inside with firebricks, which are hollowed out so as to form flues running parallel to the axis of the retort. The heating gas is fed through a gland into burners which project into the flues, the whole heating system and the burners rotating with the furnace. The fuel is introduced into the retort by a helical conveyor at the one end; at the other end the semi-coke drops into the space *h*, and thence into trucks, whilst the gases and tar vapours find an outlet through *h* and the tube *z*. It is not apparent for what purpose the furnace is lined inside, and is made to rotate. The author is under the impression that this retort is already surpassed by the much simpler German rotary retorts.

### (2) *Internal Heating.*

The obvious idea to effect carbonisation by the aid of superheated steam directly forced through the layer of coal was many years ago adopted for brown coal by Ramdohr. Ramdohr called the tar which he produced in this way "steam-tar," but the process did not find favour at the time.

Franz Fischer and W. Gluud originally tried to distil coal by means of superheated steam combined with slight external heating. They abandoned these experiments (unpublished) in favour of their rotating drum with steam distillation.

*Superheated Steam as Heating Agent.*—Lamplough <sup>76</sup> constructed a device in which he effects carbonisation entirely by means of superheated steam.

The retort (Fig. 36) consists of an iron tube, tapering towards the top, and lined with bricks for the purpose of heat insulation. Superheated steam enters at the bottom and is uniformly distributed over the cross-section of the retort by means of a perforated plate. The steam passes through the coal and leaves the retort together with the distillation gases and the tar vapour. At first, the steam is only superheated sufficiently to expel primary tar, but later on it is heated to 800°, in order to facilitate the formation of ammonia.

There is no doubt that steam is the most suitable direct heat carrier, because it can be separated from the products of distillation by simple cooling, so that these products are obtained in an undiluted form. Yet such a process would probably be very expensive for a complete tar recovery. It is not sufficient merely to cool the large amount of steam necessary to 100°; the steam must be condensed to water to make the extraction of benzine possible.

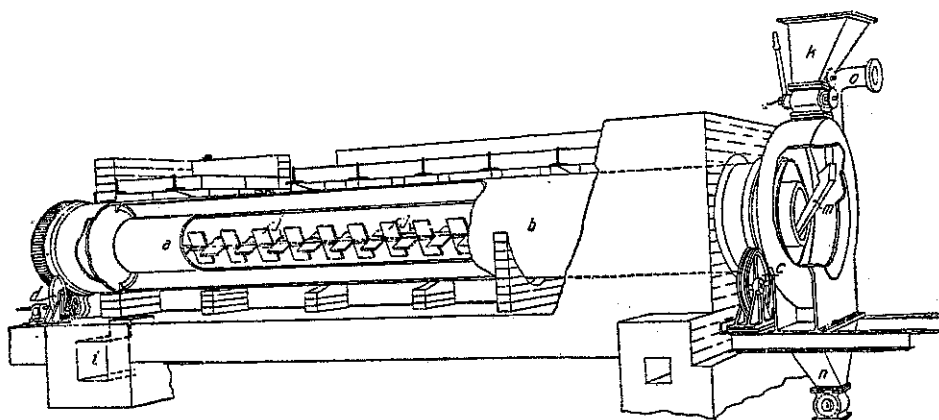


FIG. 32.

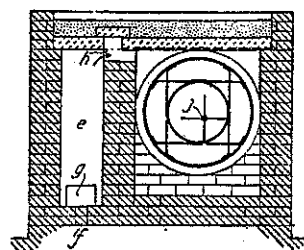


FIG. 33.

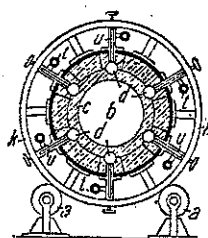


FIG. 35.

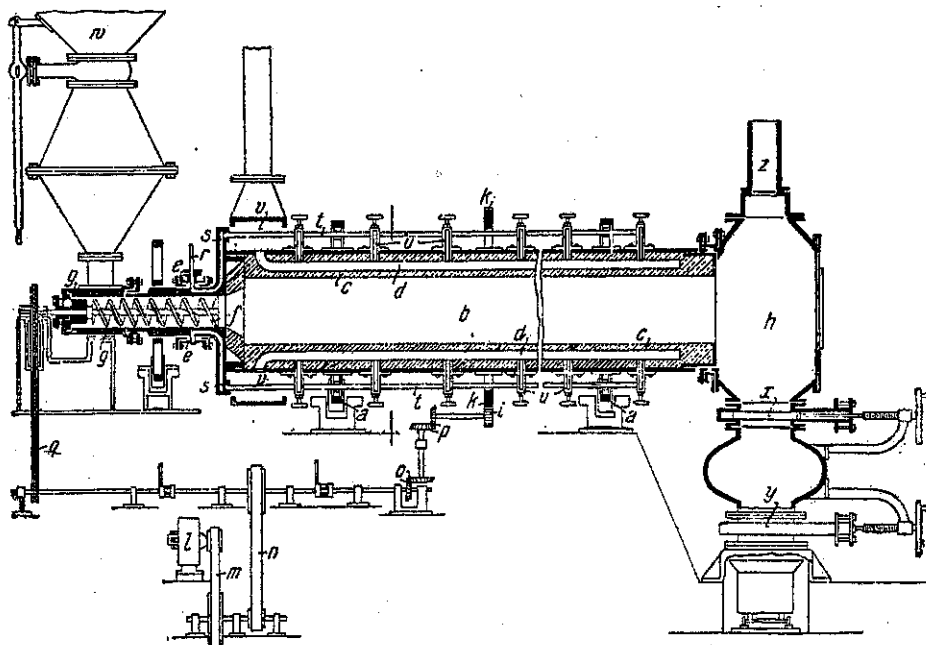


FIG. 34.



This involves further steam raising, a combination which even with good heat exchange means a large expenditure of fuel and of cooling water.

*Hot Producer Gas as Heating Medium.*—Maclaurin <sup>77</sup> effects carbonisation by means of hot generator gas instead of superheated steam. A small gas generator (Fig. 37) is directly joined to a shaft furnace, so that the gas passes through a conduit from the upper zone of the generator under the grate of the shaft furnace. The hot gas, made from a low-grade fuel in the generator, carbonises the coal charge in the shaft furnace. The carbonisation products of the coal mix with the generator gas, and their liquid constituents are separated by condensation. The semi-coke is drawn off at the bottom of the shaft furnace. This method of carbonisation, by means of unburned

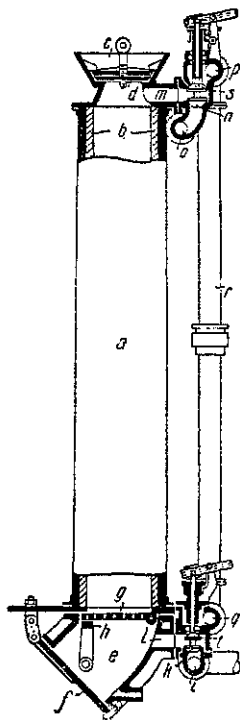


FIG. 36.

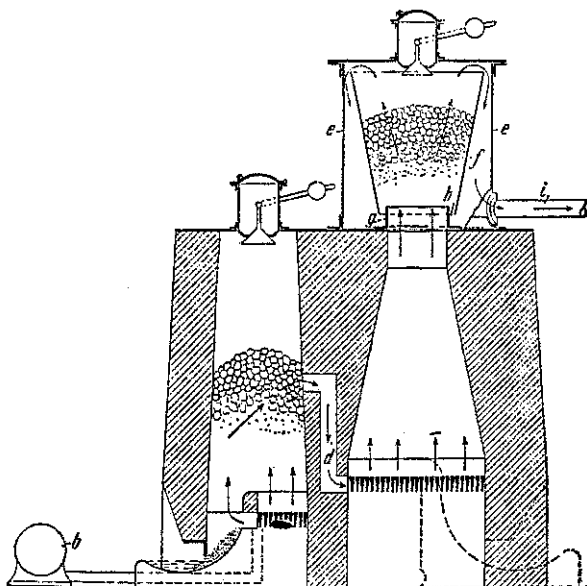


FIG. 37.

generator gas, comes close to the conditions prevailing in the carbonising generators to be discussed below. The whole difference in principle lies in that a fuel of lower grade is gasified in the place of the semi-coke in the shaft furnace. As in the carbonising generators, there is a necessity of finding an application for the generator gas which is produced in large quantities, and the recovery of the low-boiling constituents from the large volume of generator gas would probably be a matter of difficulty.

Nielsen <sup>78</sup> also makes use of the sensible heat of producer gas for the carbonisation of coal. His process differs from Maclaurin's in the fact that he employs a rotary inclined retort (Figs. 38 and 39).

The hot gas from a producer is passed by a short connection into the discharge end of a rotary retort, 27.5 metres long, consisting of two lengths of tube built up of boiler plate. The retort is designed for a throughput of 100 tons of coal per day. The inside of the retort is lined with firebrick to reduce the loss of heat by radiation. The producer gas traverses the rotary

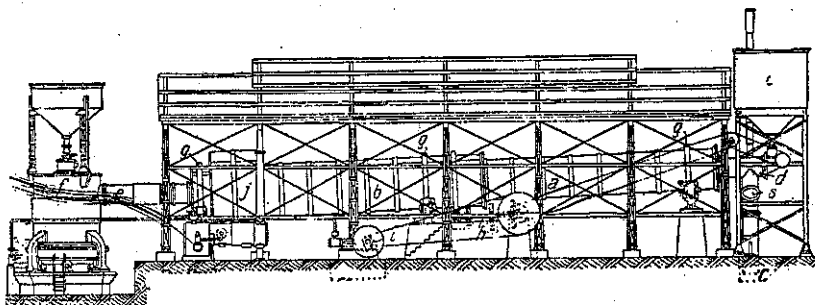


FIG. 38.

retort in counter-flow to the coal, which travels from the upper to the lower end. In order to keep the gas as free of dust as possible, the coal is charged into a trough which projects 3 metres into the retort. As the producer gas mixes with the products of carbonisation, gas is discharged at the upper end of the retort. The products always pass from the high-temperature zones,

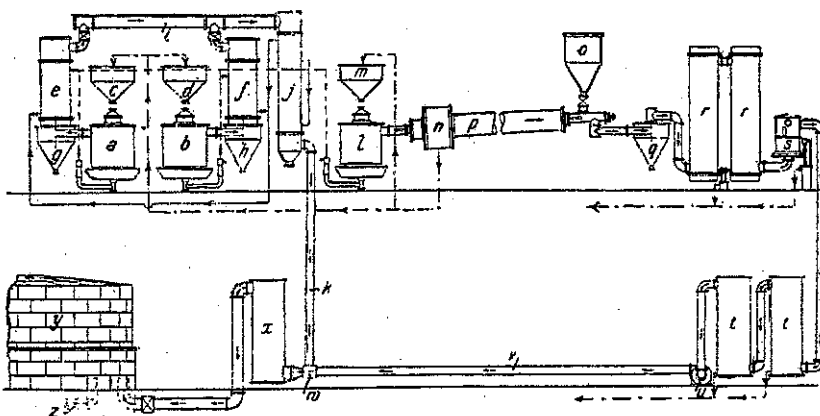


FIG. 39.

at which they are formed, to zones of lower temperature, a provision by which secondary superheating is avoided. The mixture of the two gases is taken from the outlets to the condensers and tar separators for the recovery of primary tar, benzine and ammonia, in the usual way.

*Hot Coke-oven Gas as Heating Medium.*—Sutcliffe and Evans<sup>79</sup> have conducted researches into the problem of low-temperature carbonisation, with the object of obtaining a smokeless fuel. By mixing coal rich in gas

with lean or oxidised coal they propose to improve the physical structure of coke, the various coals being ground and briquetted at high pressure without the addition of a binder. Their briquettes are described as being sufficiently hard and strong for carbonisation in high vertical retorts. Provided that a high enough compressive strength of the briquettes can be obtained, these inventors consider retorts with a daily throughput of 1000 tons possible. They propose to effect the low-temperature carbonisation of their compressed fuel by forcing hot coal gas through a perforated cylinder, axially mounted in the vertical retort so that it takes up the products of carbonisation. The gas is continually reheated in two regenerators, one of which is giving up its heat to the return gas, while the other is brought up to temperature again by the combustion of the surplus carbonisation gas, with the usual arrangement for changing over. The authors give no particulars of the recovery of oil. The proposals by Evans and Sutcliffe are mentioned, because they consider the problem of coke formation from a particular and interesting point of view.

*Carbonisation by Means of Flue Gases.*—A process which Seidenschnur<sup>80</sup> investigated and worked out jointly with the Allgemeine Vergasungsgesellschaft may become of importance for the production of tar from brown coal. Seidenschnur established, in the first instance, that cautious carbonisation of bituminous brown coal in a current of superheated steam will give a higher tar yield than that obtainable in the laboratory without the application of steam. This tar is particularly rich in oils of high viscosity, and contains, in addition, considerable proportions of undecomposed bitumen. The essential feature of this distillation is, however, that very little combustible gas is produced. He obtained 60 to 70 litres of gas per kg. of coal (briquettes), but 70 per cent. of this gas consisted of carbon dioxide with a little hydrogen sulphide. Seidenschnur considers that with this mode of tar production an appreciable liberation of valuable gas could be avoided; carbonisation might be effected by means of the products of combustion of producer gas with which the distillation gases might be wasted without causing any loss. No low-boiling hydrocarbons (benzine) are contained in the tar or gas, but they could be obtained by a subsequent distillation of the tar at atmospheric, or a higher pressure. Whether such a process would be applicable to bituminous coal is questionable, as it yields, unlike brown coal, a small percentage of low-boiling hydrocarbons which must not be lost. In an experimental plant the process is worked in the following way: gas is made in a producer from Grude coke; the producer gas is then burned in a small combustion chamber with the theoretical amount of air to a mixture of carbon dioxide, steam and nitrogen, which enters hot into the lower portion of a vertical retort charged with brown coal in briquette, or lump form. The gases leave the retort at the top together with a little distillation gas, and are

deprived of their tar in the usual fashion, the gas itself being allowed to go to waste.

I shall refer to another process of carbonisation by means of combustion gases later on, in connection with the furnaces of Pintsch, in which preliminary carbonisation in a current of flue gases takes place.

## (3) Combined Apparatus

It has long been known that in the gasification of bituminous coal in producers tar is obtained. This tar is, however, of very poor quality when taken hot from the generators, for instance, for the purpose of utilising all its sensible heat in a Siemens-Martin furnace. The lighter constituents of the tar do not separate and they are chemically changed by super-heating; the higher boiling fractions separate on the cool parts of the pipes and conduits. By contrast with hot generators a considerable quantity of good tar is obtained in Mond gas producers (Fig. 40), which for the purpose of a high yield of ammonia are run at low temperature by means of a copious supply of steam. Mond gas tar is closely related to primary tar; indeed with a fuel-bed of sufficient height a product equal to primary tar can be obtained.

Thyssen & Co., of Mülheim-Ruhr, have for some time been producing Mond gas tar which they work up for lubricants. As long as the production of primary tar in producers was restricted to "cold" generators, it did not admit of expansion.

*Hot-Run Generators Fitted with Carbonising Retorts.*—The introduction of special carbonising retorts made it possible to obtain primary tar from "hot" generators. With generators provided with these special retorts, it is desirable to keep the distillation gases and tar vapours separate from the producer gas

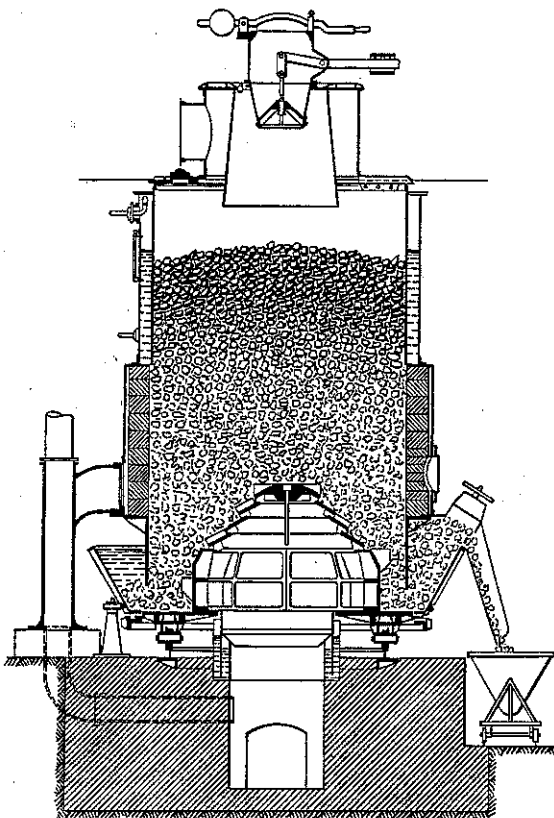


FIG. 40.

which is made in the lower zone of the generator by the gasification of the semi-coke. The producer gas can then be carried to the point of consumption, whilst the carbonisation gas passes to the tar separators. This separate collection of the carbonisation gases has the great advantage that condensation of the tar and recovery of benzine can be effected from a much smaller volume of gas, in smaller apparatus, and more completely, than if it were diluted

with many times the volume of producer gas.

If gas flame coal is thus gasified in a producer so that it has first to pass through the retort *A* (Fig. 41), in which it is heated up to  $500^{\circ}$  before it enters the shaft *B* below, and if it is left in the retort long enough, a yield of 100 kg. of tar and 50 cb.m. of gas per ton will be obtained, the gas having a heating value of about 9000 calories. On the other hand, the coal, after removal of the tar and of the gas, will yield in the producer portion proper only about 5 cb.m. of a gas of approximately 1200 calories.

During the passage of the gas through the retort, a considerable amount of water is evolved, so that, in addition to the 100 grams of tar and the 50 litres of gas from every kg. of coal charged into the retort, 0.7 kg. of semi-coke is discharged from it. This semi-

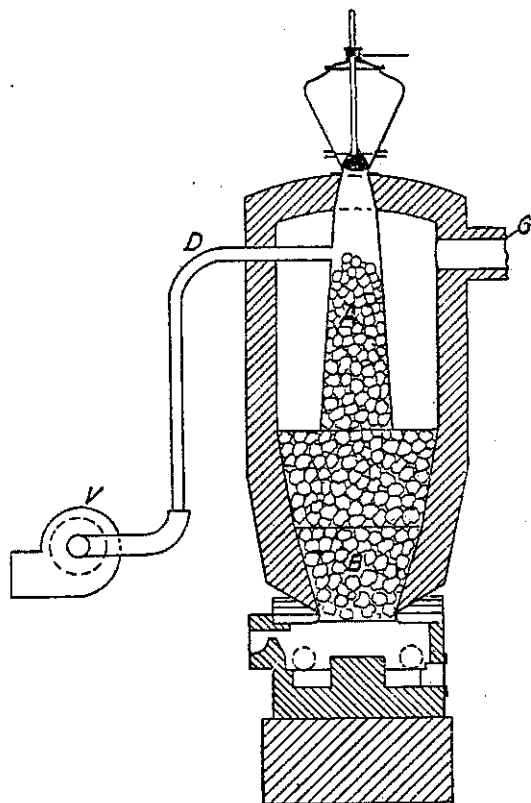


FIG. 41.

coke will then yield only 70 per cent. of the 5 cb.m., that is, 3.5 cb.m. of producer gas of 1200 calories.

The producer gas is withdrawn from the generator at *G* and can be utilised hot; the small quantity of distillation gas, which only amounts to  $1/70$ th of the producer gas, is taken off at *D*, and cooled for the recovery of tar oils and water. As the distillation gas has a calorific value of more than 9000 calories, even in the completely tar-free condition, it may be utilised not only for enriching the generator gas, but also for such special purposes as autogenous welding.

The enrichment of the producer gas cannot be pushed very far, as only

50 litres of this richer gas are available per 3.5 cb.m. of the poorer gas. In the most favourable circumstances the calorific value may rise from 1200 to 1300 calories.

The small yield of rich gas has certain advantages in the removal of the tar and the liquor. One kg. of a gas flame coal with 30 per cent. of volatiles at 500° yields 50 litres of gas and 100 grams of primary tar. From these 50 litres of gas, 100 grams of tar can be easily and quantitatively scrubbed out, including the more volatile hydrocarbons. The condensing apparatus required and the consumption of cooling water will be small. On remixing this gas, freed of tar and water (50 litres), with the large volume of hot producer gas (3500 litres), the temperature of the latter is hardly lowered. If, however, the distillation gas is diluted by drawing in producer gas, its volume is increased and its calorific value is correspondingly diminished. From this large volume of gas, the lighter tar oils and the benzine are not so easily recovered, and on remixing, the producer gas is cooled to a greater extent.

In ordinary Mond gas plants, in which the distillation products are not taken off separately, it would be necessary to extract 100 grams of tar oil per kg. of coal from 3500 litres instead of from 50 litres. The recovery of the light tar constituents becomes therefore much more difficult. The tar recovery plant must also be much larger. In practice it has been found, however, that the separate withdrawal of the gases is not conducive to the smooth working of the generator. If the heat required for the carbonisation of the coal is entirely transmitted through the wall of the retort, carbonisation does not proceed rapidly enough to keep step with the gasification of the semi-coke. Additional heat must consequently be supplied to the coal by other means. This is brought about by drawing a considerable portion of the hot producer gas through the retort, and thus utilising it for directly heating the coal. How large this portion should be can be easily ascertained by trial. The producer gas withdrawn directly must be free of tar, whilst the retort gas should contain a maximum of tar. The moisture percentage of the fuel used naturally exerts a considerable influence upon the amount of the producer gas required for complete carbonisation. The desire for a separate withdrawal of the retort and producer gas has led to a compromise, which, with respect to the recovery of the lower boiling constituents, still remains more advantageous than the combined take-off of the two gases. The first systematic experiments in this direction were made by Ehrhard and Sehmer, of Saarbrücken, and were continued by the off-shoot of this firm, the A.-G. für Brennstoffvergasung (Fuel Gasification Co.). Originally the generators were fitted with several carbonising retorts, which were replaced by an annular chamber designed by Linck, which is illustrated in Figs. 42 and 43. The annular chamber is sub-divided into compartments, which are

fed from one common hopper, below which a revolving saucer, provided with an opening, uniformly distributes the semi-coke over the cross-section of the generator. The heating of the chamber is effected partly from outside by means of the hot generator gas which surrounds the chamber, and partly from the inside, a portion of the hot generator gas being drawn through the retort. The bulk of the producer gas is available for use in a hot state for any application. With bituminous coal, about 25 per cent. of the producer gas made must be drawn through the retort; with brown coal briquettes more is required. Trials on a works scale in Upper Silesia, in the Ruhr and in the

Saar district, have proved that the tar yield was 80 per cent. of that obtainable in the laboratory.

The primary tar produced in this way is quite satisfactory, and it is stated that the additional consumption of coal to make up for the tar extracted does not exceed 10 per cent. As tar fetches a higher price than coal, the process, if carefully operated, seems to be commercially sound.

If the whole of the producer gas is cooled for tar recovery and then applied in metallurgical processes, it is very doubtful whether the same temperatures can be reached in the furnace as

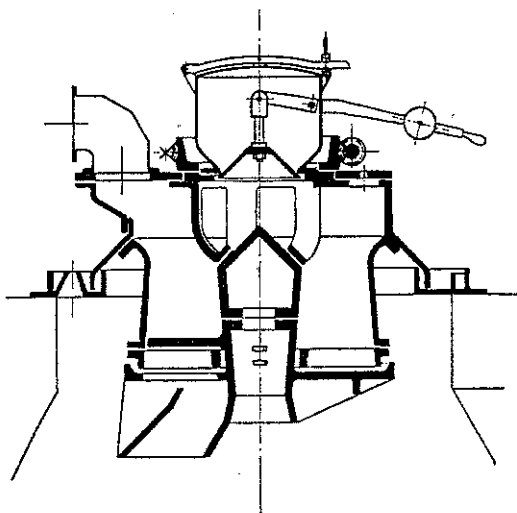


FIG. 42.

with gas still containing its sensible heat. Against this objection it must be remembered that the gas loses during condensation not only tar, but also a large portion of its water vapour. Since the water vapour in the gas acts merely as ballast, its condensation raises the calorific value of a given volume of gas. The argument that the removal of tar would considerably lower the calorific value is not quite tenable, for the tar vapours in gas leaving the generator at about  $800^{\circ}$  are already partially decomposed to permanent gas, and the absence of these decomposition products of the tar will diminish the calorific value only to a slight extent. The further objection that in the Siemens-Martin furnace a flame free of tar and soot cannot be so easily controlled, is not very serious with proper supervision. Besides, less valuable tar products might be added to make the flame luminous.

*Retorts Combined with Low-temperature Producers.*—Thyssen & Co. do not fit their gas producers with retorts, but prefer to carbonise in large rotary drums, and to gasify the semi-coke subsequently in Mond gas producers.

The Deutsche Mondgas- und Nebenprodukten G.m.b.H., on the other hand, have developed carbonising retorts fitted into their generators. These retorts are provided with mechanical stirrers which, by loosening and by mixing the coal, make for a more rapid and more complete carbonisation (Fig. 44).

A number of other generator systems might be named, working with or without carbonising retorts, which have, however, not found any general adoption.

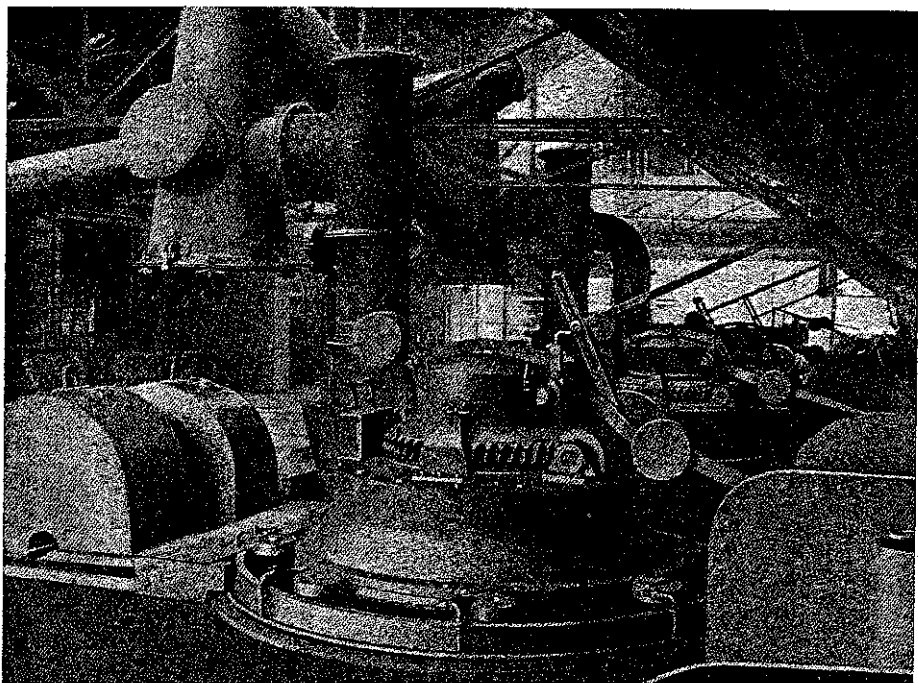


FIG. 43.

A very large plant for the recovery of tar and mineral oil from coal has been erected at Rositz, by the Deutsche Erdöl-A.-G., in which brown coal briquettes are gasified in producers. These are combined in groups of five with a common condensing plant, and they are provided with carbonising retorts, as shown in Fig. 45. The whole of the producer gas from each generator is drawn through this carbonising retort. The gas is stripped of tar, benzine and ammonia. Since their erection these producers have undergone various structural alterations. At the present time they have a rated throughput of 32 tons of briquettes per generator in 24 hours, with a yield of tar approaching that of the laboratory test. The tar production of this plant amounts at present to 35,000 tons per year, or nearly equal to that of the rest of the Central German brown coal distilleries. The tar is worked up



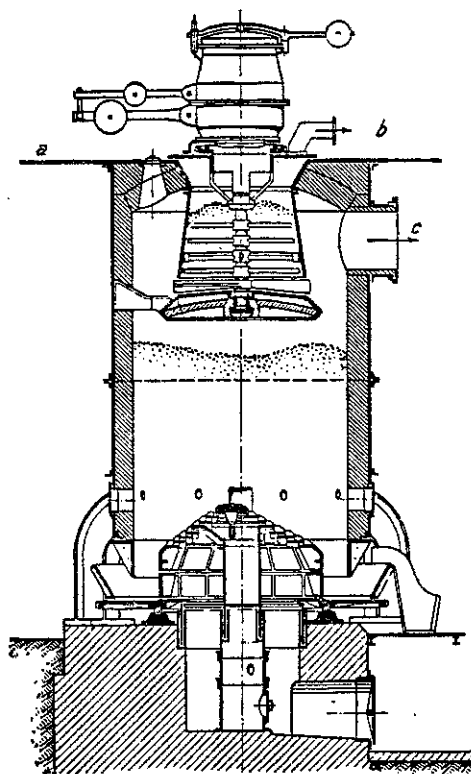


FIG. 44.

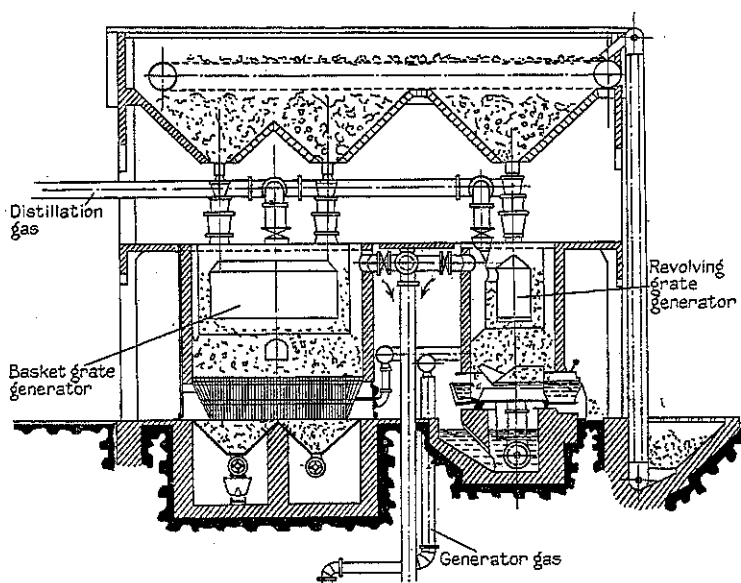


FIG. 45.

in a separate oil works into paraffin wax (candles), lubricants, fuel oils and benzene. In addition, sulphate of ammonia is produced.

A similar large plant in Lützkendorf, which has been completed, and was intended for the gasification of unbriquetted coal, has never got to the producing stage because it was found that the tar recovery from undried raw coal was not profitable.

The Dellwick-Fleischer-Wassergas-Gesellschaft, Frankfort-on-Main, has erected a water gas plant combined with tar recovery on the Tri-gas system at Mathias Stinnes Colliery. During the blow period, the blast enters at the level between the carbonising and producing zone, being directed both downwards and across the coke over an arch. The temperature in this intermediate zone is thereby raised so high that the water gas made during the run enters the layer of coal above sufficiently hot to cause an adequate degasification of the coal. The heat given by the blast must be very intense, because the amount of water gas available for the carbonisation is only a fraction of the gas made in an ordinary generator with steam and air. In the Tri-gas plant the coal gas is mixed with the water gas produced. Since the latter volume is much greater as compared with the amount of water gas simultaneously produced, the calorific enrichment of the water gas is not of a high order. 1.8 cb.m. of Tri-gas made per kg. of gas flame coal can contain not more than 50 litres of coal gas. The object of this plant was not so much the enrichment of water gas with retort gas as the direct production of water gas from bituminous coal instead of coke, together with the recovery of primary tar. The Mathias Stinnes Colliery has also begun to carbonise gas coal in a rotary retort so as to produce semi-coke and primary tar. The production of water gas from the semi-coke then proceeds much more smoothly and without caking troubles in the generator.

*Preliminary Carbonisation of Furnace Fuel.*—It has been repeatedly pointed out that the recovery of oil from bituminous coal cannot be expected to assume large dimensions as long as the daily throughput of the apparatus in use, vertical retort, rotary retort or producers, remains too small. If it were possible to carbonise the coal which is fired under the boilers of electric power stations, large quantities of tar would become available. The simplest plan seems to be to place a rotary retort in front of the fire-box, and to send the coal through this retort into the boiler furnace. The retort might be externally heated by means of the products of combustion. There is the further possibility, especially in the case of brown coal, to carbonise on Seidenschnur's principle, utilising the sensible heat of the waste gases.

To the best of my knowledge this procedure has not yet been applied. Julius Pintsch, A.-G., of Berlin, have put down a plant in the Lichtenberg Electricity Works for carbonising the fuel prior to firing it under the boilers. Gerdes<sup>81</sup> reported on this process in some detail. The fuel passes from the

bunker into a carbonising shaft mounted above a chain-grate stoker; it slowly descends the shaft while the hot products of combustion travel upward from the grate through the fuel and are withdrawn through the gas outlet into the purifier plant (Figs. 46 and 47). It is stated that a good yield of primary tar of good quality was obtained. Unfortunately the experiment had to be discontinued, owing to the closing down of the works on incorporating the town supply in a district power distribution scheme.

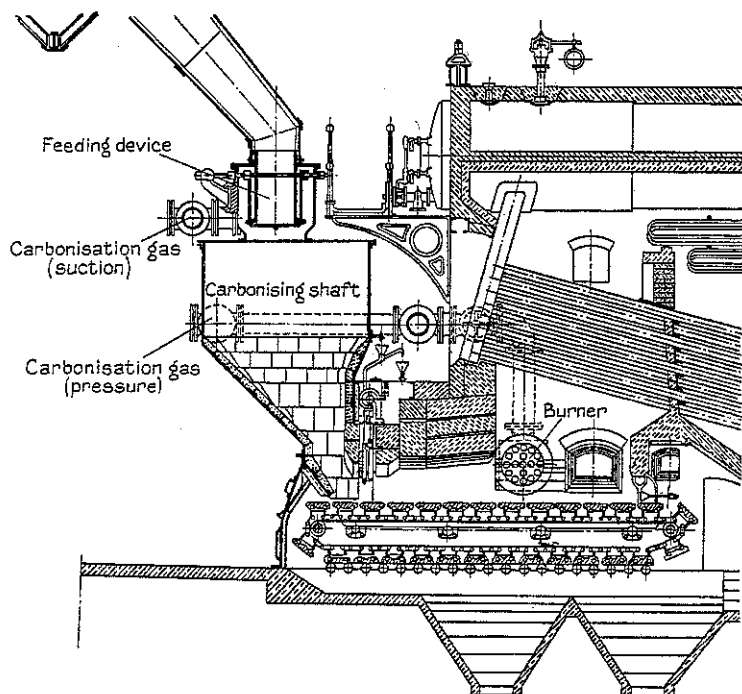


FIG. 46.

From the section on the production of primary tar, it will be recognised that the problem of its production from coal is being energetically and systematically attacked in all countries, and that the tar problem itself may be regarded as solved, but that there are still some difficulties in connection with the semi-coke and its utilisation. There can be little doubt that these outstanding questions will find a solution within the next few years.

The low-temperature carbonisation processes yield, as has been shown, chiefly heavy fuel oils, the benzene percentage being about 10 per cent. of the tar. In the Synthol process we shall find a process which can be combined with low-temperature tar production for the utilisation of semi-coke, and which yields essentially light motor spirits.

(p) THE INFLUENCE OF RETORT DESIGN UPON THE COMPOSITION OF PRIMARY TARS AND GAS BENZINES

Primary tars vary with the design of the plants, and particularly with the distribution of temperatures in the retort and the path which the tar vapours take. This question may therefore be discussed a little more in detail. Let us study the conditions of benzene evolution from coal at 300°. Fischer and Gluud<sup>82</sup> have shown that a large portion of the benzenes preformed in the coal are liberated at 300° to 350°, and that these benzenes, according to

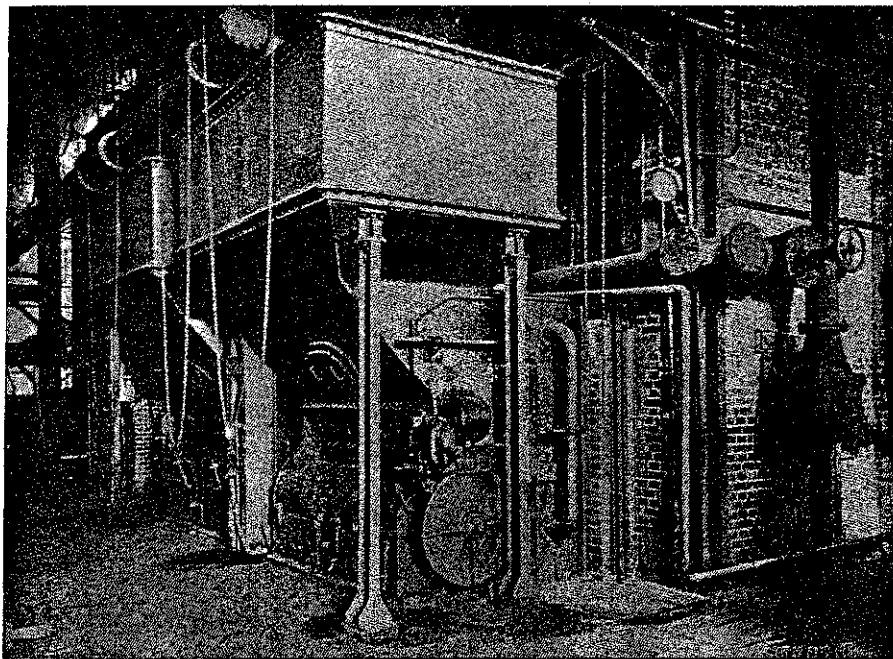


FIG. 47.

analysis, specific gravity, etc., are hydrocarbons definitely non-aromatic, but richer in hydrogen. We obtained such benzenes by heating the coal in our rotating drum, raising the temperature in one to two hours from the ordinary to 500°. The vapours appearing, say, between 300° and 350°, were at once withdrawn and condensed, before the retort had reached an appreciably higher temperature (Fig. 48).

Similar conditions prevail in a gas producer (Fig. 49). Here the benzene evolved, say, at 300°, travels upwards through the cooler descending coal without passing through a zone of higher temperature, say, of 600°, at which it might be dehydrogenated or undergo some decomposition.

Our small laboratory rotating drum was obviously not designed for continuous working. The large rotary retorts of Thyssen & Co. are designed for continuous working; the tar vapours do not flow in counter-current with the coal, and they are taken off at the coke discharge end. If the retort were to work on the counter-current principle, the conditions would be as favourable for preserving the primarily-formed compounds rich in hydrogen, as in our intermittent process or in a well-conducted producer, and the material vaporised at  $300^{\circ}$  would not subsequently be exposed to higher temperatures. Where the gas and coal run in the same direction,

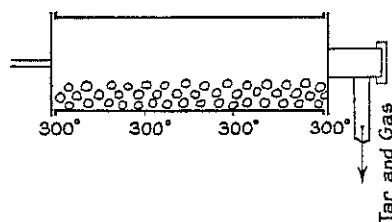


FIG. 48.

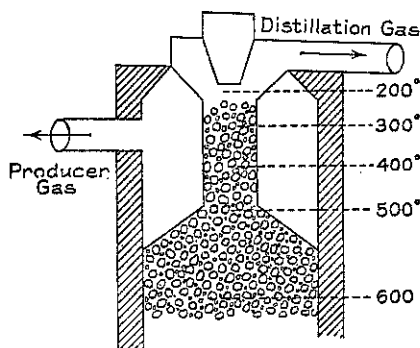


FIG. 49.

the products liberated at  $300^{\circ}$  are bound to be heated to  $500^{\circ}$  or  $600^{\circ}$  at the coke discharge end of the drum.

The benzines are not the only constituents susceptible to thermal change. Fischer and Gluud have shown that primary tar is modified to a considerable extent even by repeated distillation at ordinary pressure, and particularly when heated to  $600^{\circ}$ .

In the rotary retort of Fellner and Ziegler, as in those of Thyssen & Co., the tar vapours are withdrawn at the same end as the coke, as indicated in Fig. 50. I am informed that the reason for this practice lies in the difficulty of tar discharge at the cold end of the retort. It is conceivable that under these conditions the high-boiling constituents will be re-deposited upon the cold coal to be returned to the hot zone. Still, it

should be possible to design a plant on the lines of Fig. 51, in which the products of distillation are withdrawn through a lagged pipe from a zone of about  $300^{\circ}$  towards the cold end of the retort. Whether or not this would be feasible in practice, I am not able to judge.

Published descriptions, now coming forward, of low-temperature tars produced in rotary retorts of the type shown in Fig. 50, prove that these products have passed through temperatures from  $500^{\circ}$  to  $600^{\circ}$ , and no longer accord in their composition with those Gluud and I obtained in the first instance. The discrepancies cannot be explained by the differences in coals carbonised, but must be sought in superheating phenomena in the retorts.

Naphthenes are known to undergo dehydrogenation at  $500^{\circ}$ , and Jones<sup>83</sup> has shown that *cyclo*-hexane, methyl-*cyclo*-hexane and tetrahydro-naphthalene

begin to be decomposed at or about this temperature. *cyclo*-Hexane yielded benzene and higher olefines, the balance being gas, chiefly hydrogen. The other naphthenes examined behaved similarly. Since there are naphthenic and partly hydrogenated aromatic hydrocarbons contained in the middle and higher fractions of low-temperature tar, it is not surprising that tars produced in too hot a retort, though not containing naphthalene (which is not formed below 700°), yet contain considerable amounts of aromatic hydrocarbons produced by dehydrogenation. In order to avoid confusion it would be desirable to give in future descriptions of primary tars the results of their detailed examination on the lines set out on p. 31. It will then be found

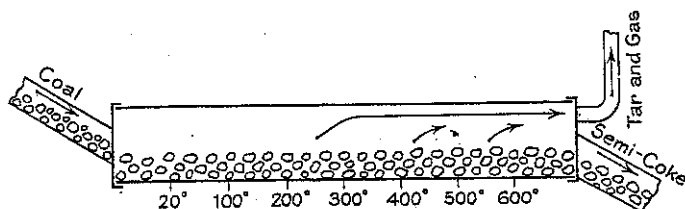


Fig. 50.

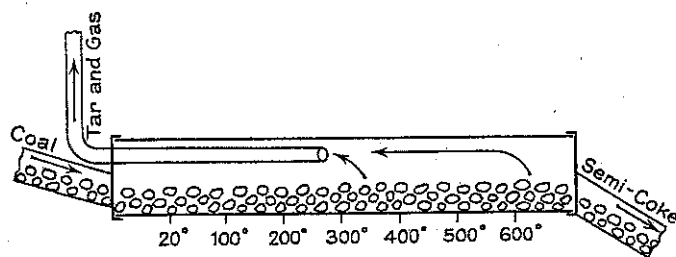


Fig. 51.

if they are appreciably aromatic that they also show signs of superheating, and that the hydrocarbon fraction 200° to 300° has a specific gravity of rather more than 0.95 at 20°. The lubricating oils being likewise of naphthenic character, such tars will not contain as much lubricating oil as a true primary tar. The lubricating oils change, slowly at 300° and very rapidly at 500°, into cracked products poorer in hydrogen.

#### (g) THE INFLUENCE OF COAL DRYING ON THE OIL RECOVERY

With bituminous coal of low moisture content drying is not as important as with brown coal, which as mined frequently contains 50 to 60 per cent. of water. The following remarks relate therefore chiefly to brown coal and even more to peat which contains 90 per cent. of water; to coal, perhaps, in special cases. Although the drying of brown coal requires the same expenditure of energy, whether performed separately, or in the carbonising

plant, there is a certain inclination to saddle the retort or generator with this extra duty. What are the disadvantages of such a procedure? Starting from *dried* brown coal, the distillation yields, in addition to tar and gas, a little liquor, which is evil smelling and objectionable owing to its phenol and sulphur compounds, of low ammonia content and therefore of no commercial value. It may cause difficulty by contaminating ground water and polluting rivers. If the coal is carbonised undried, and drying is effected in the carbonising apparatus, the liquor gets diluted by the original moisture of the coal, and the quantity of the malodorous and objectionable water to be disposed of is materially increased. These drawbacks are avoided if the coal is first passed through an independent dryer at a temperature considerably below that of carbonisation.

In a continuous rotary retort it is quite possible to dry brown coal, as mined, and to carbonise it in the hotter parts of the retort, supplying the heat required from outside sources; in producer working the conditions are different. The heat capacity of the hot producer gas rising from the gasification zone is mostly insufficient for the drying and carbonisation of the upper layers of coal, or for heating them sufficiently to carry the tar vapours from the generator. For this reason regular carbonisation of raw brown coal in a producer is not possible, and still less if the coal is of an earthy character and tends to clog the fuel-bed. This will particularly happen when steam is condensed in the upper layers by lack of heat in the gas. The tendency in future will therefore be to dry the raw brown coal in separate dryers, and thus avoid the dilution of the gas liquor with the natural moisture of the coal. With the rotary system this can be easily effected by heating a separate rotating drying tube with the products of combustion from the carbonising furnace. The steam liberated will be mostly allowed to escape, though it may be collected if desirable. Lump brown coal should be dried down to 15 per cent. moisture, and then charged still warm into the generator. Smaller earthy coal should be duly dried and briquetted. The cost of the treatment cannot be as high as is often asserted. The main expenditure of energy in briquetting goes towards the drying; the pressing takes a fraction only. The energy spent on drying is afterwards saved in the generator, the capacity of which becomes much higher.

It is sometimes stated that it is profitable to run a producer on moist coal, because water vapour is necessary for the gasification, and that it would protect the tar vapours from decomposition. Both these arguments are unsound. The temperature of the fuel-bed of a producer increases from the top downwards. Water is vaporised in the uppermost layer. By the time the coal gets into the carbonising zone the moisture has been expelled; this is certainly the case when the semi-coke has passed into the gasification zone. To charge the generator with moist coal therefore serves no useful purpose.

The suggestion that the tar is protected by the water vapour might have some foundation in the case of a continuous rotary retort not worked on the counter-current principle. In this case the water vapour actually travels through the whole tube and pushes the tar vapour in front of it. It condenses afterwards, together with the liquor from the carbonisation, and increases its volume in the undesirable manner described.

From the scientific standpoint only one objection can be raised against the preliminary drying of the coal. It has been shown<sup>84</sup> that moist coal gives the highest tar yield, and that all dry coals yield less tar, especially when dried by contact with the air.

It may be presumed that, so far as the tar yields are concerned, there is little difference between moist and air-dried brown coal as long as the action of atmospheric oxygen is limited to a few days' storage. Graefe has shown that *prolonged* storage in the air at ordinary temperature has a definite oxidising effect, and influences the tar yield. The same phenomena occur in a shorter time if coal is exposed to atmospheric oxygen at higher temperatures, for instance, when the coal is dried at 105°. In our experiments the samples of moist coal yielded, after drying in the air at 105°, in three cases from one-third to two-fifths less tar than the moist coal as mined; whilst air-dried coals, or those dried at 105° in a current of CO<sub>2</sub>, gave a quarter to one-tenth less tar than the moist samples. Thus, for example, Kayna coal gave :

moist as mined	.	.	.	.	.	15%	primary tar
air-dried	.	.	.	.	.	11%	" "
dried in CO <sub>2</sub> at 105°	.	.	.	.	.	11%	" "
dried in air at 105°	.	.	.	.	.	8.5%	" "

These phenomena, observed in the laboratory, may become very important in the drying of brown coal for briquetting on a large scale. Here, moist coal is also heated to higher temperatures in contact with the air, and is therefore modified so as to diminish the tar yield. It is of importance particularly where briquetted coal is gasified in producers for the production of primary tar. Taking Kayna coal as an example, with a preliminary drying down to 10 or 15 per cent. moisture, the tar yield should not be as low as 8.5 per cent., though it might be depressed to 11 per cent. after ordinary air drying. How far a modification of the conditions of drying will prevent the loss of tar due to internal oxidation, *e.g.* by drying either for longer periods at lower temperature or for shorter periods at higher temperature, is an open question on which some data should be available in works practice. In any event, it would be of advantage to dry, not in air, but in a gas free of oxygen or at any rate poor in oxygen, such as flue gases.

The reduction of the tar yield caused by the preliminary drying is not



as serious as it appears at first. It includes mainly the less valuable constituents of phenolic character, whilst the yield of hydrocarbons, per unit weight of coal carbonised, remains the same. If the tar produced is to be worked up for paraffin wax, lubricating oils and fuel oils, the reduction caused by preliminary drying of the coal is not a disadvantage. Graefe pointed out that tar obtained from coal after long storage makes up in quality what it has lost in quantity, and confirmed this assumption experimentally.

To summarise this section, moist coal should be dried in separate apparatus before being carbonised. It should be briquetted if of earthy character, as is done, for instance, in the large works of the Deutsche Erdöl A.-G., at Rositz, where a raw brown coal is used in generators.

### (r) UTILISATION AND WORKING-UP OF PRIMARY TAR.

#### 1. *Direct Utilisation of Primary Tar*

Crude primary tar from coal has a calorific value of about 9000 and could no doubt be used as liquid fuel. At the ordinary temperature it is fluid, but rather viscous, the viscosity being greater the less completely the low-boiling constituents were condensed. This tar will, however, hardly be applied as liquid fuel as it is too valuable for that. Containing the low-boiling constituents, its setting point will be near  $+4^{\circ}$ . The setting point might be lowered by allowing the paraffin wax to crystallise, and removing it in the usual way. Crude primary tar from coal may also be used in large internal combustion engines of the Diesel type. In its general applicability this tar stands mid-way between coke-oven tar and crude petroleum. Owing to its viscosity (50° Engler at 20°) crude primary coal tar may act as a lubricant to a very limited extent. In order to obtain good lubricating oils the tar must be worked up by the methods used in the petroleum industry.

Crude primary tar thickens by evaporation of the low-boiling constituents and hardens by oxygen absorption; it can therefore be used as a protective paint for wood. With an admixture of zinc dust the tar gives a grey-green coating, which on iron soon dries and forms a good protective. Such preparations are, however, inferior to linseed oil paints.

The crude primary tar from brown coal, owing to its high setting point of  $+35^{\circ}$  (ointment consistency at ordinary temperature), is not suitable for the above-mentioned purposes, and should be worked up into more valuable products.

#### 2. *Working-up of Primary Tar by Distillation* <sup>85</sup>

##### *Chemical Changes on Distillation.*

The essential superficial difference between the primary tar from bituminous coal on the one hand, and from brown coal on the other, is that the former

is fluid whilst the latter is semi-solid. Thus the primary tar which we prepared in the rotating drum <sup>21</sup> from gas flame coal of Lohberg Colliery had specific gravity 1.00 at 25°, 0.982 at 50°, and setting point + 3.5°.

The coal had the following composition :

<i>Proximate Analysis.</i>		<i>Ultimate Analysis.</i>	
	Per cent.		Per cent.
Moisture . . . . .	1.8	Carbon . . . . .	80.8
Volatile matter . . . . .	37.2	Hydrogen . . . . .	5.5
"Fixed Carbon" . . . . .	59.3	Nitrogen . . . . .	1.9
Ash . . . . .	1.7	Sulphur . . . . .	0.7
	100.0	Oxygen by diff. . . . .	9.4
		Ash . . . . .	1.7
			100.0

The primary tar from Saxon brown coal (coke yield 51 per cent.) was semi-solid at the ordinary temperature, its setting point was + 37°; in the liquid state its specific gravity was 0.853 at 50°.

That the primary tar from bituminous coal is liquid, whilst that from brown coal is semi-solid, is easily accounted for by the fact that the former is rich in liquid phenols, but poor in paraffin wax, and that the coal contains already liquid hydrocarbons which pass into the tar. From brown coal, on the other hand, only solid constituents can be extracted,<sup>86</sup> such as montan wax, etc.

TABLE XVI

Yields.	Primary tar from gas flame coal.	Primary tar from Saxon brown coal.
	Spec. grav.: At 50° 0.982 ,, 25° 1.000 Setting pt. + 3.5°	Spec. grav.: At 50° 0.853 Setting pt. + 37°.
1. <i>Distillation</i>		
Distillate . . . . .	83%	91% (dry)
Coke . . . . .	10%	4%
Spec. grav. of distillate . . . . .	{ at 50°: 0.948 at 25°: 0.971	{ at 50°: 0.869
Setting point of distillate . . . . .	- 19°	+ 28°
2. <i>Distillation</i>		
Distillate . . . . .	94.4%	96.2% (dry)
Coke . . . . .	3.0%	1.2%
Spec. grav. of distillate . . . . .	{ at 50°: 0.942 at 25°: 0.946	{ at 50°: 0.864
Setting point of distillate . . . . .	below - 19°	+ 15°
<i>Cracking at 600°</i>		
Distillate . . . . .	70%	73.5% (dry)
Coke . . . . .	very little	0.8%
Spec. grav. of distillate . . . . .	at 25°: 0.990	at 50°: 0.878
Setting point of distillate . . . . .	below - 19°	- 13.5°

On distilling brown coal a tar is produced which, in addition to paraffin wax, contains a fair amount of undecomposed montan wax and other solids which cause the higher setting point. For the further study of the behaviour of these two primary tars on distillation the following methods were used:—

*Bituminous Coal.*—The primary tar from a gas flame coal was first distilled at ordinary pressure from an iron still filled to half its capacity. It was to be expected that a large portion of the high-boiling constituents, comprising the highly viscous and unstable lubricating oil, would be destroyed. Table XVI shows that distillation left 10 per cent. of coke and gave 83 per cent. of an oily distillate. The loss of 7 per cent. includes water and gas formed. The specific gravity of the distillate was lowered, and the setting point dropped to  $-19^{\circ}$ .

A distillation, on identical lines, of the distillate obtained, yielded only 3 per cent. of coke and 94.4 per cent. of distillate, with a loss of only  $2\frac{1}{2}$  per cent.; the specific gravity of the second distillate was still lower, and the setting point was below  $-19^{\circ}$ .

Finally, the second distillate was once more distilled from an iron retort, and passed through an iron tube charged with broken brick heated to  $600^{\circ}$ . The yield of distillate was then only 70 per cent. owing to the strong decomposition, accompanied by evolution of gas; the specific gravity increased, but the setting point remained below  $-19^{\circ}$ .

These experiments indicate that the primary tar of gas flame coal becomes more and more fluid by distillation at atmospheric pressure, and that it assumes an extraordinarily low setting point which would render it very suitable as fuel oil and for other purposes.

*Brown Coal.*—Brown coal primary tar was then treated in the same way. It left in the first distillation only 4 per cent. of coke and yielded 91 per cent. of distillate, of a setting point  $+28^{\circ}$ .

The second distillation gave 1.2 per cent. of coke and 96.2 per cent. of distillate, of setting point  $+15^{\circ}$ . Primary tar from brown coal is therefore likewise converted into a liquid oil by repeated distillation at ordinary pressure. The setting point is more markedly affected by destructive distillation at  $600^{\circ}$ . 73.5 per cent. of distillate, of setting point  $-13.5^{\circ}$ , was obtained with strong evolution of gas. The specific gravity was slightly higher than originally, but not as much as in the case of the primary tar from bituminous coal.

These experiments demonstrate that, in the production of primary tar, both from bituminous and brown coal, the setting point may be lowered at will by subsequent distillation at atmospheric pressure.

In the commercial production of such tars in generators, it should also be possible to operate the plant so as to get tar of any viscosity and setting point, *i.e.*, of any desired degree of decomposition. The least decomposed

tars are those of the highest setting point, provided that the temperature has not risen above 600°, and that all the constituents of the crude gas, which are liquid at the ordinary temperature, have been condensed. If the low-boiling constituents remain uncondensed, the consistency of the tar will, of course, change according to the temperature of the gas leaving the condenser. Instead of an oily tar, under these conditions one containing viscid clots may be obtained.

Only limited percentages of unaltered lubricating oils may be expected in a tar distilled at ordinary pressure and at 600°. Brown coal tar in particular, if by repeated distillation or a corresponding thermal treatment is produced as an oil, liquid at the ordinary temperature, is not likely to contain valuable lubricants. Unsaturated compounds in either tar can, by subsequent heating to the proper temperatures, with or without catalysts, be converted by condensation or polymerisation into products of lubricating oil character.

The deduction to be drawn from these experiments and considerations is that the recovery of viscous oils from the primary tars of bituminous and brown coal demands a cautious treatment, and the application of lower distillation temperatures such as are attained by the use of superheated steam or vacuum.

#### *Working-up by Distillation at Ordinary Pressure*

In the distillation at ordinary pressure, the constituents of tar chiefly affected by chemical change are those boiling above 200°. The products boiling below 200°, crude benzine, are obtained as readily by ordinary distillation as by steam or vacuum distillation. The oils which boil between 200° and 300° are obtained in much larger proportions by ordinary distillation than by steam distillation. The reasons are that the fractions boiling above 300°, and in particular the highly-viscous lubricating oils, are decomposed into constituents of lower boiling points, some of which boil between 200° and 300°. Two litres of primary tar from Lohberg gas flame coal, prepared in the laboratory rotating drum, were distilled from a fire-heated iron still.<sup>87</sup> A light oil fraction was collected below 225°, and a motor oil fraction from 225° to 300°; the temperature was then raised to 325°.

The products were: 120 grams of water, 448 grams of light oil, 517 grams of motor oil, 438 grams of fraction 300° to 325°, and 450 grams of pitch.

The motor oil produced had too low a flash point, being below 60°. In order to raise it the oil was redistilled up to 225°, and the distillate obtained was added to the light oil. The yield of light oil thereby rose to 524 grams, whilst that of the motor oil was diminished to 441 grams. At the same time the flash point of the motor oil rose to 71°. The further examination of these products gave the following results:—

Light oil: flash point below 35°; yield 26 per cent. of tar used; calorific

value, gross 9734 cal., net 9194 cal.; analysis, carbon 80.52 per cent., hydrogen 9.99 per cent.

Motor oil: flash point 71°; yield 22 per cent. of the tar used; calorific value, gross 9132 cal., net 8630 cal.; analysis, carbon 83.06 per cent., hydrogen 9.29 per cent. Specific gravity at 20°, 0.988; viscosity at 20° = 5° Engler; setting point, below + 3°, with stirring, - 12°.

Fraction 300° to 325°: yield 22 per cent.; 9 grams of paraffin wax were filtered from this fraction; the filtrate had at 50° a viscosity of 5° Engler. The removal of the phenols lowered the viscosity of the residual hydrocarbons to 1.9° Engler at 50°. The hydrocarbons did not deposit any more paraffin wax at room temperature.

Pitch: yield 22.5 per cent. of the tar used. The pitch remained hard when heated in the water-bath; gradual softening without decomposition set in at 125°. In order to lower the softening point of this product, it was regenerated in the following way: 100 grams of pitch were melted, and gradually small portions of the fraction 300° to 325° (after removal of paraffin wax) were stirred into the fused mass. After adding 30 grams of oil the softening point had dropped to 80° (Krämer-Sarnow). The regenerated pitch had the following properties: Specific gravity at 20° = 1.190; calorific value, gross 8619 cal., net 8271 cal.

Distillation products obtained without further chemical treatment are tabulated below:—

TABLE XVII

	In tar.	Boiling range.
Light oil . . . . .	26%	Below 220°
Motor oil . . . . .	22%	220-300°
Phenolic lubricating oils . . . . .	22%	300-325°
Paraffin wax . . . . .	0.5%	—
Pitch . . . . .	22.5%	Above 325°

This treatment yielded fairly crude products; the most valuable constituents, the viscous lubricating oils, were destroyed in this distillation.

Lubricating oils may be regenerated by treating the phenolic lubricating oil boiling from 300° to 325° in the following way:—

*Regeneration of Lubricating Oil.\**—All distillates above 300° were freed of paraffin wax and then, by treatment with 10 per cent. caustic soda, of phenols. The hydrocarbons were separated from water by centrifuging and then heated in an iron pot to 265°. 627 grams of this material yielded some water and 32 c.c. of a light yellow oil. The residue showed at 50° a viscosity of 2°

\* According to Engler's method.

Engler. The forerunnings and residue were then remixed and kept in an autoclave at 355° to 360° for 48 hours. Twenty-four hours later the autoclave scarcely showed any pressure; after 48 hours the pressure had risen to 20 atm. After cooling the autoclave, the gas copiously liberated was allowed to escape; it burned with a bright non-smoking flame. The oil made was again heated in an iron pot; at 80° a light oil began to come over; 75 c.c. were collected up to 265°. This oil was of a reddish-yellow colour and an intense green fluorescence. The remaining oil boiling above 265° had at 50° a viscosity of 33·4° Engler (against 2° Engler before), a very remarkable change which was also apparent from its colour, which had turned into a deep dark brown; the setting point was + 7·5°. This oil, being free of phenols, and the product of a thickening process, should be suitable for various lubrication purposes.<sup>88</sup>

*Distillation at Ordinary Pressure and Chemical Treatment*

The fraction 150° to 300° of the primary tar from bituminous coal, obtained by distillation at atmospheric pressure, and the corresponding fraction of brown coal tar are treated in exactly the same way,<sup>89</sup> i.e., by first removing the phenols with 5 per cent. caustic soda and then the bases with dilute sulphuric acid. They both yield mixtures of hydrocarbons of close similarity, which by fractionation and refining with concentrated sulphuric acid can be separated into practically the same products. These products are tabulated below.

TABLE XVIII

	In tar.	Boiling range.
Tar benzine . . . . .	5·0%	Below 150°
Solar oil . . . . .	5·5%	150-220°
Cleaning oil . . . . .	1·0%	220-250°
Gas oil . . . . .	8·8%	250-300°
Neutral lubricating oil . . . . .	6·0%	300-325°
Paraffin wax . . . . .	0·5%	—

To these yields must be added the phenols extracted by caustic soda from the fraction 150° to 300°, amounting to 24 per cent. of the tar. Another portion of the phenols originally in the tar is in the pitch residue which amounts to 37 per cent. of the tar. As pointed out above, the hydrocarbons of primary tar from bituminous coal give the same products (solar oil, cleaning oil, yellow oil, red oil, gas oil, etc.), as those from brown coal tar. Particularly striking and complete is the resemblance between the solar oils from the two kinds of coal. Since solar oil in suitable burners is used as a lamp oil, the production of oil for illuminating purposes from bituminous coal is

proved. The two oils tally in colour, specific gravity, ultimate composition, calorific value and viscosity, provided that the tar has really been prepared under true low-temperature conditions. A superheated tar is not likely to yield such a solar oil. Further details of these experiments will be found in *Abh. Kohle*, 1918, 3, 46.

*Working-up of Primary Tar by Means of Superheated Steam and Chemical Treatment*<sup>90</sup>

In order to prevent the decomposition of the viscous oils in primary tars care should be taken not to exceed a temperature of 300°. One mode of achieving this, by means of superheated steam, will be first described. Starting from the primary tar of gas flame coal, the phenolic constituents may be first extracted with caustic soda. As the tar contains about 50 per cent. of phenols, its volume will thus be halved. From the remaining hydrocarbons (neglecting the small amount of bases) the tar benzine is distilled off, up to 200°. Superheated steam is then introduced, when non-viscous oil comes over, until the vapour temperature reaches about 190°; as the temperature rises viscous oils are obtained; finally at 240° the products become resinous.

Results from fat coal are similar; the products have a better appearance, but the drawback is that the fat coal yields relatively little tar. The yields are summarised in Tables XIX and XX.

TABLE XIX

Fat coal. 100 kg. coal gave about 3 kg. tar.	
	%.
Valuable viscous oils (lubricants)	15.2
Paraffin wax . . . . .	0.4
Non-viscous oils . . . . .	33.5
Phenols . . . . .	14.0
Resins . . . . .	4.2
Pitch . . . . .	19.2
Loss and water . . . . .	13.5
	100.0

TABLE XX

Gas coal. 100 kg. coal gave about 10 kg. tar.	
	%.
Valuable viscous oils (lubricants) .	10.0
Paraffin wax . . . . .	1.0
Non-viscous oils . . . . .	15.0
Phenols . . . . .	50.0
Resins . . . . .	1.0
Pitch . . . . .	6.0
Loss and water . . . . .	17.0
	100.0

Owing to the presence of paraffin wax, the viscous oils obtained by simple distillation have a high setting point. This may be lowered by removing the paraffin wax. By dissolving the oils in acetone, cooling the solution to -10°, filtering the paraffin wax on the pump, evaporating the acetone and fractionating the wax-free oil with the aid of superheated steam, lubricating oils of the properties summarised in Table XXI were obtained.

the separation of paraffin wax; badly de-paraffined lubricating oils from petroleum show the same defect. Deficiencies in other properties, like oxidisability, etc., are also due to careless distilling, and the true history of such an oil would probably show that it had been driven over at high temperature and with strong decomposition, instead of having been submitted to a very cautious distillation as described.

"As long as products which have not been treated with care can find a ready sale and command high prices, it is intelligible that the preparation of primary tar is not carried out with the requisite attention. As soon as the competition of superior products makes itself again felt, the inferior products from primary tar will be forced from the market, and this contingency is rapidly approaching. The manufacture of superior products will then needs follow, the feasibility of which has been sufficiently emphasised.

"The economic necessity for improved methods will be found when the price of primary tar drops and therefore the raw material itself does not form an easy source of profit. The margin between raw material and finished product will then become wider and create an incentive for improvements in refining. Complaints of the quality of products from primary tar at present, I consider a good sign which can only make for improvement and will do away with the easy profits and the unnaturally high prices. It is not correct to ascribe the fault to the character of the tar, or the principle of its production; it really lies in the want of care bestowed upon the working-up of the products."

Gluud's arguments must be agreed with, but should be supplemented by recent experience in the primary tar industry. The objection that lubricants cannot be made from it must not be advanced against true primary tar. The difficulty lies in that the commercial products are frequently not true *low-temperature* tars, but are partly dehydrogenated, as explained in the section on "Influence of Retort Design." Even the most skilful distiller cannot get good results from such tars.

Viscous lubricants being high-priced products, the oil from coal will best be submitted to some hydrogenation process, as used in fat hardening or in tetraline manufacture. The process of Bergius will hardly be applicable, as it requires a temperature above 300°, where decomposition into non-viscous products takes place.

*Examination of Primary Tars for Lubricating Components.*<sup>s2</sup>—In testing a tar for its content of viscous oils, the following method may be resorted to if high flash points are not wanted, and in the absence of suitable apparatus for distillation in superheated steam.

The tar is first submitted to steam distillation in order to remove the more volatile constituents. The residue is well shaken with two or three times its volume of petroleum ether (boiling range 90–100°). The viscous oils are dissolved, leaving behind the bulk of acid and asphaltic compounds. The



solution is then shaken in turn with alkali, water, dilute sulphuric acid and again with water, and so freed of its acid, basic and resinous substances. The petroleum ether solution is evaporated at reduced pressure and finally at  $100^{\circ}$ , leaving as residue the viscous oils which mostly congeal to ointment consistency on account of their paraffin wax content. For the separation of paraffin wax the product is mixed with several times its volume of acetone, and cooled to  $-10^{\circ}$ ; the paraffin is filtered off, and the acetone evaporated in a vacuum, raising the temperature to  $100^{\circ}$ . The viscous oil obtained still contains traces of acetone and petroleum ether.

The industrial working-up will be on somewhat different lines from that of our gas flame coal experiments in Tables XIX and XX. The whole tar is distilled and the phenols extracted from some selected fractions only. Under certain conditions partial extraction of the most acid phenols, with a restricted amount of caustic soda, will be preferable; the phenols which pass over together with the lubricating oils are also very viscous, and even more so than the hydrocarbons of the same boiling range. The non-viscous oils serve as liquid fuel, and after refining possibly as solvents. The highest fractions are of a resinous character and contain paraffin wax.

Freshly distilled, they are of yellow colour, which quickly darkens. The proportion of pitch left in the still can be reduced at will, by forcing the resinous compounds over. If it should be possible to remove from the resinous portion those constituents which cause the darkening, or to prevent it by hydrogenation, very valuable products would be obtained.

Improvement by means of hydrogenation both of resins and lubricants is one of the problems of the future. The difficulty is that the usual catalysts are rapidly poisoned by sulphur-containing materials, while hydrogenation without catalyst, according to Ipatiew or Bergius, is inapplicable owing to the high temperature required. Something might perhaps be achieved by electrolysis of the solutions or emulsions with cathodes, for example of lead, at high voltage.\*

It has already been explained that primary tar from brown coal is altered by distillation at ordinary pressure, owing to the decomposition of the viscous constituents. It will be shown below that this tar is also a source of highly viscous lubricants when treated with care.<sup>92</sup> For this purpose a fair quantity of primary tar from Central German brown coal was prepared in the rotating drum. This tar differs materially from commercial brown coal tars. The yield is 100 per cent. of that given by analysis, whilst in the production of brown coal tar in the Rolle retort 60 per cent. is usually taken as a basis (Scheithauer, "Shale Oils and Tars," 2nd edition). A commercial brown coal tar has a setting point of  $+15^{\circ}$ ; the primary tar prepared from the same coal showed a

\* de Hemptinne's "Voltol" process, using silent electric discharges, need hardly be considered here.

TABLE XXI

*Condensed from 170° to 193° (temp. of vapour 210–235°)*

65 grams medium viscous lubricating oil:

Flash point . . . . .	152°
Setting point . . . . .	–12°
Viscosity at 20° . . . . .	7.2° Engler
„ at 50° . . . . .	1.73° „

*Condensed from 193° to 205° (temp. of vapour 235–255°)*

100 grams viscous lubricating oil:

Flash point . . . . .	182°
Setting point . . . . .	–5°
Viscosity at 20° . . . . .	19.2° Engler
„ at 50° . . . . .	5.4° „

*Condensed at 205° (temp. of vapour 255–265°)*

90 grams very viscous lubricating oil:

Flash point . . . . .	194–195°
Setting point . . . . .	+4.5°
Viscosity at 50° . . . . .	28.3° Engler
„ at 100° . . . . .	1.9° „

Characteristic of these viscous oils are their deep golden-red colour and feeble green fluorescence; further, their pleasant aromatic, yet strong fatty smell. The smell resembles somewhat that of oils directly extracted from coal (see Chapter I, Extraction). The quantity of viscous oils also recalls the conditions of the extraction. Fat coal yielded 3 per cent. of tar, and the tar itself contained 15 per cent. of viscous oil, or 0.45 per cent. of weight of coal. Gas flame coal yields 1 per cent. of highly viscous oil. The yields are of the same order of magnitude as those by extraction of coal with anhydrous sulphur dioxide, and it is quite feasible that the oil which existed preformed in the coal should be found in the tar distillate, if all superheating has been avoided during carbonising and in distilling; the characteristic smell will at once attract attention. The oils obtained by distillation also contain constituents formed by the decomposition or de-polymerisation of the bitumen in coal.

If a solution of 100 grams of the viscous oil in petroleum ether is extracted with concentrated sulphuric acid, 10 grams of a viscous, quite colourless oil are obtained. But it is not necessary to push the acid treatment so far, and it is never done in practice. It suffices to remove the compounds particularly liable to resinification. As regards the value of the lubricant from primary tar, Glund <sup>91</sup> wrote as follows:—

“Very discordant opinions are held by practical men regarding the lubricating oil obtainable from primary tar. The responsibility for failures is mostly ascribed to the tar, but should be more properly placed on the distiller. Too high a setting point indicates that proper attention has not been paid to

setting point of about  $+38^{\circ}$ . This is due to the higher percentage of solid products (paraffin, montan wax, etc.) which have undergone less decomposition, owing to the lower temperature and to the quick removal of the vapours from the drum by the steam current. The results of the working-up of the primary tar from brown coal by means of superheated steam are summarised in Tables XXII and XXIII.

TABLE XXII

*Central German Brown Coal rich in Bitumen (Carbonising Coal)*

100 kg. coal (dry basis) gave 24 kg. primary tar.			% of tar.
I. Viscous oils composed of :			
(a) highly viscous oils :	$(V_{20} = 67.0^{\circ} \text{ Engler})$	.	1.73%
(b) medium " " :	$(V_{20} = 11.4^{\circ} \text{ " "})$	.	13.01%
(c) slightly " " :	$(V_{20} = 5.4^{\circ} \text{ " "})$	.	2.47%
total : $(V_{20} = 13.5^{\circ} \text{ Engler}, V_{50} = 2.85^{\circ} \text{ Engler})$			17.21%
			17.2
II. Solid products (hard and soft paraffin wax, etc.)			29.4
III. Non-viscous oils (free from creosot)			28.9
IV. Tar acids			10.5
V. Resinous substance			2.2
VI. Pitch.			3.2
VII. Loss			8.6
			100.0

TABLE XXIII

*Results of Fractionation with Superheated Steam of Viscous Oils*

	$V_{20}$	$V_{50}$	Setting point.	Flash point.	Tar yields.
below $180^{\circ}$	below $5^{\circ} \text{ Engler}$	—	—	—	2.41%
$180-210^{\circ}$	$5.28^{\circ} \text{ "}$	$1.68^{\circ} \text{ Engler}$	$-12^{\circ}$	$135^{\circ}$	5.65%
$210-235^{\circ}$	$45.4^{\circ} \text{ "}$	$6.02^{\circ} \text{ "}$	$-4.5^{\circ}$	$199^{\circ}$	3.61%
$235-255^{\circ}$	—	$49.5^{\circ} \text{ "}$	$+21^{\circ}$	$176^{\circ}$	3.79%

#### *Working-up in a High Vacuum*

Primary tar from brown coal and its products are at present made on a very large scale by the Deutsche Erdöl A.-G. Works at Rositz,<sup>93</sup> in high-vacuum plants designed and built by the Brünn-Königsfelder Maschinenfabrik. "The distillation is effected in large continuous stills of 40 cb.m. capacity, arranged in groups of eight; the tar, freed of a certain fraction, flows into the next still from which the next fraction is taken."—"The temperature difference between two adjacent stills amounts to about  $15^{\circ}$ . Distillation begins at the tempera-

ture at which the preheated raw material enters the first still, *i.e.*, at about 200°, and finishes at 320°. Owing to the high vacuum of 680 mm. a goodly proportion of the tar passes over. The off-takes between the stills must be of ample diameter so as to equalise the vacuum in all the stills; otherwise there might be serious disturbances in the circulation of the tar from still to still.

“The tar enters the higher still, which is at the lowest temperature, and runs from it into the second, which is mounted 30 cm. lower; the difference between the levels of the first and the last still thus amounts to  $7 \times 30 = 210$  cm. Each still yields two fractions, one coming down in the preheater, and one in the condenser. Apart from the light distillates which are taken up in the preheaters, sixteen fractions are thus obtained. All these fractions are not kept apart; for the further working-up, the light and the heavy distillates free of paraffin wax, as well as those containing wax, are combined in a smaller number of groups.”—“The stills are heated by means of producer gas which is taken from the producers in which the tar is produced. Owing to the high vacuum, the lubricating value of the hydrocarbons of the brown coal tar is much better preserved than with the former method of working. The producer tar is anyhow less decomposed than the brown coal (Schwel-) tar, and by further distilling it with every care, oils are obtained of a lubricating value which could not be obtained with ordinary brown coal tar. The Deutsche Erdöl A.-G. has put brown coal tar lubricants on the market, which though as regards lubricating power, purity, smell and cold point are not quite equal to the corresponding petroleum products, yet have done a great deal towards the reduction in imports of lubricants into Germany from other countries. Two such lubricating oils had the following properties :—

TABLE XXIV

	Machine oil I.	Machine oil II.
Viscosity at 50° . . . . .	3-4° Engler	4-5° Engler
Ignition point . . . . .	165-180°	170-185°
Specific gravity . . . . .	0.970-0.980	0.970-0.985
Solidification point . . . . .	+7° to +8°	+7° to +8°

“The large quantities of paraffin wax which are obtained in the working-up of the brown coal producer tar are also important, as the existing supplies from the brown coal carbonising industry do not meet the home consumption. The methods of production and refining of paraffin wax have also been changed from those formerly customary in the brown coal industry.”

The Gesellschaft für Teerverwertung, of Duisburg-Meiderich, has erected a plant for working-up primary tar from bituminous coal on the high vacuum system. An exhibition of its products formed part of the Heating Exhibition at Essen in 1922.

## 3. Separation and Utilisation of Phenols

*The Disadvantages of Phenols and their Corrosion of Metals*

The particular applicability of aliphatic hydrocarbons of high boiling points in internal combustion engines of the Diesel type is due to the decomposition of the injected oils by heat, which takes place more readily the larger the molecule. For this reason kerosene has a lower ignition point than benzene.\* The larger kerosene molecules form, by the action of heat, scission products of olefinic character which are more oxidisable and inflammable. To a certain extent the hydro-aromatic hydrocarbons share this property; they also are subject to scission, or at any rate split off hydrogen. On the other hand, aromatic compounds, with which the phenols found in primary tar must be classed, are highly resistant to heat. They are decomposed above red heat only, and then into carbon (soot) and hydrogen. For that reason a Diesel engine cannot be run on phenols, unmixed with more easily ignitable substances. It is therefore clear that gas oil from brown coal tar, which is poor in phenols, is more suitable for this purpose than the corresponding fraction of primary tar from bituminous coal, almost half of which consists of phenols. The presence of phenols is objectionable when they are present in large quantities. In that case they may have to be removed, entirely or in part, unless it is

\* The spontaneous ignition point must not be confused with the flash point. Whilst the flash point indicates to which temperatures an oil must be heated so that the layer of vapours above the oil is ignited by a small flame, the ignition point marks the temperature at which drops or sprays of the oil, falling or injected into air, spontaneously catch fire. The ignition point is important for Diesel engine oils. The most recent data are tabulated below:—

TABLE XXV

Fuel.	Ignition point °C.	
	in oxygen.	in air.
Petroleum distillates: Benzine . . . .	272	333
Kerosene . . . .	251.5	432
Gas oil . . . .	254	358
Crude oil: Californian . . . .	262	420
Shale oil: Motor oil . . . .	253	333
Coal tars: Primary tar . . . .	307	508
Horiz. retort tar . . . .	454	—
Coke-oven tar . . . .	495	—
Tar distillates: Xylene . . . .	484	—
Toluene . . . .	516	—
Benzene . . . .	566	—
Coke-oven tar oil . . . .	478	—

The ignition points are considerably higher in air than in oxygen. The ignition point of primary tar approaches that of petroleum more closely than that of coke-oven tar; the latter has a relatively high ignition point, like all aromatic hydrocarbons. It is noteworthy that the high-boiling gas oil has a lower ignition point than the low-boiling benzine, whilst the sequence of flash points is reversed (Daiber, *Zeitschrift des Vereins deutscher Ingenieure*, 1921, 65, No. 50).

expedient to reduce their concentration sufficiently by the admixture of petroleum products.

The behaviour of phenolic oils must also be studied for other reasons, in particular as to the corrosion of the metal of the engines. The different opinions expressed do not as a rule allow any definite conclusions, because the circumstances are not stated; for instance, whether the corrosion was observed when hot, in the presence of water or of air. It appeared, therefore, useful to study the behaviour of these oils in contact with the different metals used, under conditions favouring corrosion.

Ehrhardt and Pfeiderer <sup>94</sup> investigated the corrodibility of different metals by such oils in the presence of atmospheric oxygen and water. The primary tar oil which they applied had a boiling range of 150–270°, and contained about 40 per cent. of phenols. The oil was first saturated with water by shaking; the water not taken up was removed. The metals to be studied were used in the form of strips of sheet metal, or else in lumps. In order to ensure a strong reaction, the specimens were enclosed in glass tubes with the oil and air, and were kept agitated on a shaking machine during daytime for four weeks.

TABLE XXVI

Metal.	Loss of weight mgm./sq. cm.	Metal.	Loss of weight mgm./sq. cm.
Copper . . . . .	6.5	Lead . . . . .	1.1
Brass . . . . .	0.6	Aluminium . . . . .	0.0
Nickel-silver . . . . .	0.9	Tin plate . . . . .	0.22
Zinc . . . . .	1.2	Sheet iron . . . . .	0.51
Galvanised iron . . . . .	0.73	„ „ pickled . . . . .	0.04
Nickel (wire) . . . . .	0.09	Ferro-silicon (18%) . . . . .	0.0
Nickel-plated brass . . . . .	0.17	V2.A steel (Krupp) . . . . .	0.0

According to Table XXVI aluminium, ferro-silicon and V2.A steel are not attacked by phenolic oils at ordinary temperature. For tubes and sheets, aluminium should therefore be used; for rods and bolts, V2 steel; and for castings, silicon-iron. Iron and nickel were also found to be very resistant. Cast iron was not examined; it is likely that it would hardly be corroded, and that it would behave like the pickled black sheet. It is not certain to which constituent the corrosion is really due; apart from phenols, sulphur compounds must be considered. For the practical problem it was less important to ascertain which constituents have a corrosive action than which metals would resist it under all conditions. If the corrosive ingredients are really among the phenols, they would probably be those which are somewhat soluble in water. It might then suffice to remove these by treatment of the primary tar oils with superheated water.

*The Utilisation of the Phenols*

Before proceeding to discuss the various possibilities of recovering the phenols from the tar oils, which must be done cheaply, their particular mode of application must be considered. In view of the high content of tar acids and the fact that carbolic acid, at present the most valuable, only occurs in negligible proportions (see p. 41), their removal and utilisation is of the highest importance for the working-up of primary tar, especially that from bituminous coal. It may be recalled that the gas flame coals which are richest in tar yield primary tars with nearly one-half of all fractions consisting of tar acids.

In the absence of other applications, the tar acids may be utilised as liquid fuel. Their use as impregnating oils is doubtless more profitable. For this purpose, the higher boiling phenols, which are not soluble in water and therefore not liable to be washed out of the wood by rain and moisture, are the most suitable. The phenols may be condensed with formaldehyde to resins similar to bakelite,<sup>95</sup> for which there is a considerable demand. Their manufacture on a large scale is impeded by the insufficient supply of formaldehyde and consequently its high price. As soon as a cheap method of preparing large quantities of formaldehyde from methane or carbon monoxide is found, a large-scale conversion of phenols into bakelite will be possible. It would be of particular value to convert the phenols into useful fuels, since this is the purpose for which the production of primary tar is largely undertaken. That this is at present within the range of possibility will be demonstrated in one of the following chapters.

*Methods of Separation of Phenols hitherto in Use*

The simplest way of recovering the phenols from the distillates of a primary tar, of the fractions of which they may make up to 50 per cent. or more, consists in shaking the oils with dilute caustic alkali and separating the aqueous alkali solution. Such a method of working is easy in the laboratory, but would be expensive on a large scale owing to the high cost of caustic soda. The alkali, after use, must be recausticised with lime, which is quite feasible, but undesirable. This is the way at present applied in works practice; the phenolate solutions are decomposed with carbon dioxide, sodium carbonate formed being reconverted into caustic soda.

Attempts to separate the oils by means of formic acid,<sup>96</sup> which is a good solvent for phenols, but hardly dissolves hydrocarbons at all, are successful in the laboratory, but out of the question in practice, as concentrated formic acid is too costly and moreover awkward to handle. Formamide behaves similarly, but is also too expensive.

Glycol and glycerin are solvents for phenols,<sup>96</sup> but not for hydrocarbons. One might dissolve the phenols in glycerin, and then dilute the glycerin solution

with water, when the phenols separate; this would involve concentration of the glycerin solution with unavoidable losses, which makes the process uneconomical.

More advantageous is Krey's extraction with aqueous alcohol, which dissolves the phenols preferentially though not exclusively. This process is in constant use in the brown coal carbonising industry in plant designed by Kubierschky.

On mixing liquefied carbon dioxide under pressure with primary tar oil, two layers are formed; the upper layer consists chiefly of carbon dioxide and, strangely enough, hydrocarbons, whilst the lower contains mainly phenols. The separation is by no means complete, but might be adequate when repeated. The possibility of recovering and recompressing carbon dioxide quantitatively is a point in favour of this process, but the high pressure of 60 atm., at which it must be operated, is against it.

A peculiar reaction is observed when gaseous hydrochloric acid is passed into primary coal tar. The experiment is successful only with the tar itself, not with the oil fraction. Within a few minutes the tar separates into a thickish black paste and a light-coloured more fluid oil. The action becomes noticeable with as little as 0.5 gram of gaseous hydrochloric acid in 50 grams of tar; even a smaller quantity of acid would probably be sufficient. On centrifuging, the acid tar separates readily and sharply from the more mobile oil, in proportions of 60 per cent. of acid tar to 40 per cent. of thin oil. On extracting the separated oil with caustic alkali, the volume reduction indicated 15 to 18 per cent. of tar acids against more than twice that amount in the untreated tar.

The impression is gained that the acid tar is a better solvent for the phenols (and possibly for oxygen compounds in general) than the thin oil. The distribution ratio of the phenols is therefore such that the phenols pass mostly into the acid tar, whilst the thin oil is deprived of phenols.

A check experiment in which 2 c.c. of concentrated hydrochloric acid was applied per 50 grams of tar, in the place of the gaseous acid, gave the same result after a short while on a shaking machine. The distribution ratio between acid tar and thin oil after centrifuging was the same as in the experiment with gaseous hydrochloric acid. The phenol content of the thin oil was diminished to the same extent as in the previous experiment.

The oil purified with gaseous hydrochloric acid gave rise to a renewed deposition of solid resinous compounds when subsequently shaken with a little concentrated sulphuric acid.

A sample of fresh primary tar, shaken with a few drops of concentrated sulphuric acid, gave a similar deposit as with gaseous hydrochloric acid, though the oil was perhaps less fluid. Whether in this case the phenols accumulated in the acid tar was not ascertained; nor whether the lubricating oils of the tar were to be found in the acid tar, or in the thin oil.

It would be useful to continue these experiments. The acid tar might be



used several times, or the separation might be effected by the addition of acid tars from other sources. For it is probable that the acid tar produced, has a greater solvent power for the oxygenated constituents of primary tar, than for the hydrocarbons. A separation might also be attempted by dissolving other solids in the tar which are soluble in the phenols, but insoluble in the hydrocarbons. The hydrocarbons would then be replaced in their solution in the phenols by the other solute.

It has been found <sup>97</sup> that solutions of sodium sulphide may also be used for extracting the phenols from the low-temperature oils, and that this extraction will take place without an appreciable liberation of hydrogen sulphide. On passing hydrogen sulphide into the extract, phenols are precipitated, and a solution of sodium hydrosulphide (NaHS) is formed. This solution, on boiling with phenolic oils, dissolves the phenols with evolution of hydrogen sulphide. A combination of the two processes would therefore allow us to utilise the NaHS solution, over and over again, for extracting the phenols. Simple as this method appears, there is the disturbing influence of some other substance present in a small proportion in the tar oils, evidently of polybasic character (perhaps a penta- or hexa-phenol), and of an extraordinarily strong reducing power.

#### *The Recovery of the Phenols by Means of Superheated Water* <sup>98</sup>

Whilst carbolic acid can be readily extracted from oils by means of hot water, this is not possible with the phenols in primary tar, as they are homologues of phenol which are little or not at all soluble in water. If a phenol containing fraction of primary tar, *e.g.*, fraction 200° to 300°, of gas flame coal tar which contains nearly 50 per cent. of phenols, is heated in an autoclave with an equal quantity of water to 200°, with or without stirring, the cresols and the xylenols are largely dissolved in the superheated water, the oil having given up part of its phenols to the water forming a layer above the aqueous solution. This shows that the cresols and xylenols, which are scarcely soluble in water below 100°, are soluble to a considerable extent in water superheated to 200°.

On cooling the autoclave, the phenols separate again from the aqueous layer as their solubility diminishes with falling temperature. The drops of phenols forming in the oil do not sink to the bottom but rise, being still hot and specifically lighter than the aqueous layer. In consequence they redissolve in the layer of oil floating on top. If this is not taken into account and the contents of the autoclave are drawn off at the bottom, one must not be surprised to find no indication of separation, as expected on the strength of the higher specific gravity of cresols and xylenols at ordinary temperature.

The failure of the separation is, therefore, due to the difference in the coefficients of expansion of cresols and water,<sup>99</sup> cresols being lighter than water at temperatures of 200° to 300°. Another method was therefore tried.

The autoclave was so modified that the aqueous layer could be withdrawn at a temperature of 200°. For this purpose a high-pressure water-cooled condenser made of steel was fixed at the bottom of the autoclave, having a reducing valve at its outlet. The autoclave was again charged with the same quantities of primary tar oil and water; it was then closed and heated to 200° for 15 minutes. The autoclave was not allowed to cool, as in the first experiment, but connection was made with the high-pressure condenser, and the reducing valve was opened. A milky liquid was discharged, from which some drops of phenols began to separate and accumulate at the bottom of the receiver, as a heavy oily layer below the water. A test showed that the phenols were almost entirely soluble in caustic soda, proving that it should be possible to extract almost pure phenols from primary tar oils by means of superheated water.

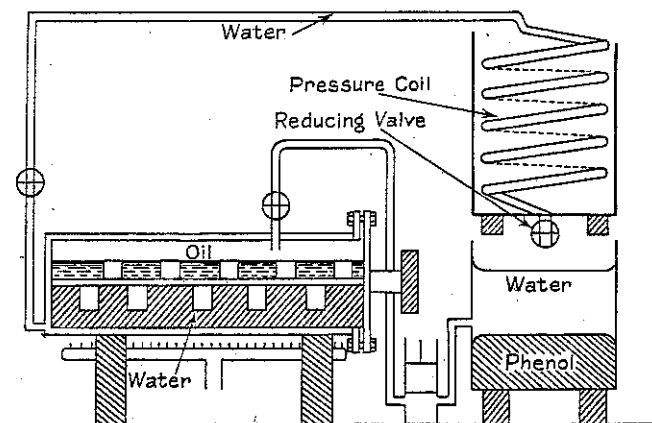


FIG. 52.

For works use, the process must, of course, be made continuous as regards both the feed and the discharge of the oils, water and the solution of phenols. We have been able to solve this problem on the small scale on which we were working with respect to the water feed.

A small high-pressure pump was fixed at one end of the horizontal autoclave by means of a copper capillary tube; by this, water was forced into the apparatus during the experiments. If the stirrer was used, the apparatus was mounted at an angle of about 6°, the pump being at the higher end, and the outlet valve at the lower end. In order to allow layers to form at this end, while stirring, the three last blades of the stirrer (see fig., *Abh. Kohle*, 1919, 4, 19) were removed. In the same way, oil might be introduced continuously from the other side and withdrawn from the water inlet side. In the industrial adaptation of such an apparatus the question of heat economy must be considered, and provision should be made for preheating the water entering the apparatus by means of the hot liquid discharged.

(1) *Experiments with Stirring.*—For these experiments rotary retort tar

from gas flame coal of Graf Bismarck Colliery was used, the fraction selected being 200° to 300°, containing 55.3 per cent. of phenols. The autoclave was charged with 1.5 litres of oil and 1.5 litres of water, heated to 225° and kept at that temperature for 10 minutes with agitation. The water for extraction was pumped in at the rate of 2 litres per hour; a total of 4.5 litres of pure water was used and circulated, after the phenols were settled and had been withdrawn. The aqueous solution of phenols was collected in portions of 1 litre. The temperature was maintained as far as possible at 250°; the speed of stirring

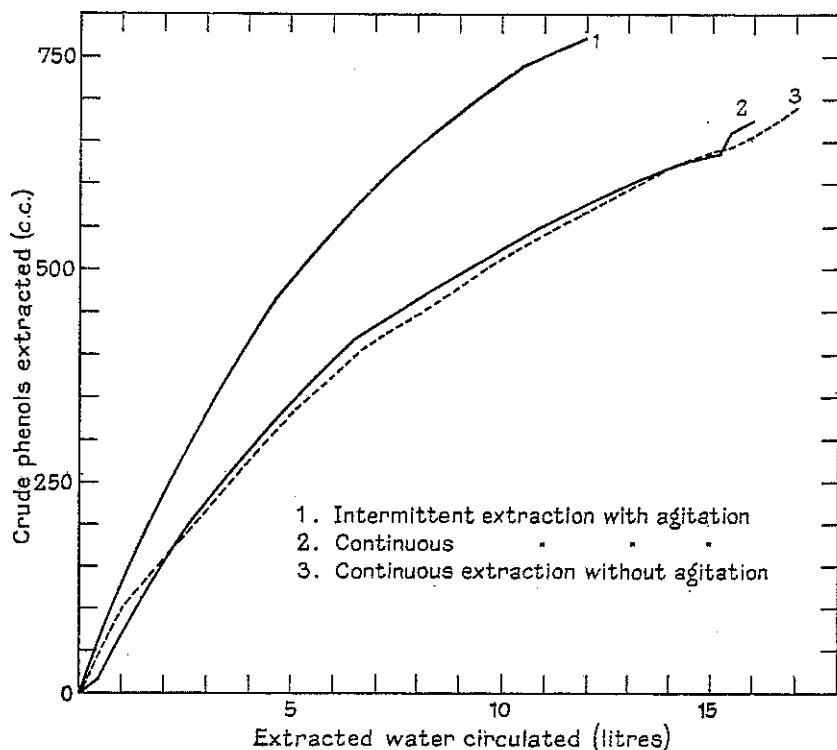


FIG. 53.

was about 120 r.p.m. After  $7\frac{1}{2}$  hours' extraction, during which altogether 15 portions of 1 litre each were collected, 635 c.c. of crude phenols had been extracted with a phenol content ranging from 86 to 96 per cent. The 1.5 litres of aqueous phenol solution still remaining in the autoclave were then withdrawn, yielding a further 30 c.c. of phenols. Renewed extraction with 1.5 litres of fresh water, with stirring, yielded another 12 c.c. of phenols, so that a total of 677 c.c. was obtained. In the autoclave 660 c.c. of oil now remained, containing only 16.1 per cent. of phenols. Of the 1.5 litres of oil used, there were 163 c.c. missing. Most of that remained dissolved in the water used for extraction; the rest was lost. The specific gravity of the oil had dropped from 0.984 down to 0.943, owing to the elimination of the relatively heavy phenols.

(2) *Experiment without Stirring.*—1.5 litres of the fraction 200° to 300° of primary tar from Graf Bismarck Colliery and 1.5 litres of water were heated to 225° in the horizontal autoclave, and kept at this temperature for 40 minutes. Water was then circulated. The volume of fresh water this time amounted to 3.5 litres. After collecting 16 lots of 1 litre each, the 1.5 litres of water left in the autoclave were drawn off. A total of 695 c.c. of crude phenols was thus extracted, containing 94 to 98 per cent. of phenol, *i.e.*, considerably more than in the experiment with stirring. 730 c.c. of oil remained in the autoclave; this had a phenol content of 18.8 per cent. The specific gravity had dropped from 0.984 to 0.947.

Fig. 53 shows clearly that in continuous experiments at the selected rate of circulation, the extraction proceeds just as quickly without stirring as with stirring. Curve 1 further shows that extraction in steps with equal quantities of water yielded a somewhat larger amount of phenols. Therefore, in the continuous extraction, the solution withdrawn was not quite saturated. This drawback might be obviated either by working at a slower rate, or by making the pressure-tube longer.

(3) *Further Experiments without Stirring.*—We then applied continuous extraction to a number of commercial phenolic oils, particulars of which are tabulated below. Experimental arrangements and rate of circulation were the same as in the previous experiment.

TABLE XXVII

*Continuous Extraction of Commercial Oils without Stirring*

Used: 1.5 litres oil, 4.5 litres water

1	2	3	4	5	6	7	8
Expt. No.	Kind of oil.	Phenol in oil before extraction. %	Number of Extracts.	Total crude phenols extracted. c.c.	Phenol in individual crude extracts. Vol. %.	Oil residue in autoclave.	
						c.c.	Phenol content. % by Vol.
1	Fraction 200–300° from primary tar of Graf Bismarck Colliery.	55.3	16 × 1 l. 1 × 1.5 l.	695	94–98	730	18.8
2	Fuel oil 180–310° from primary brown coal tar, Rositz.	19.8	10 × 1 l. 1 × 1.5 l.	156	95.5–97.5	1245	9.8

In the extraction of fraction 200° to 300° of the primary tar from gas flame coal (Experiment 1),\* the phenol content, after pumping-through 12 times its volume of water, was reduced from 55 to 19 per cent. The extracted crude phenols contained hardly any hydrocarbons. A similarly favourable result was obtained in the extraction of the fuel oil fraction 180° to 300° from Rositz primary brown coal tar. In that case only one-half of the 20 per cent. of phenols remained in the oil. It should be pointed out at this stage that for most

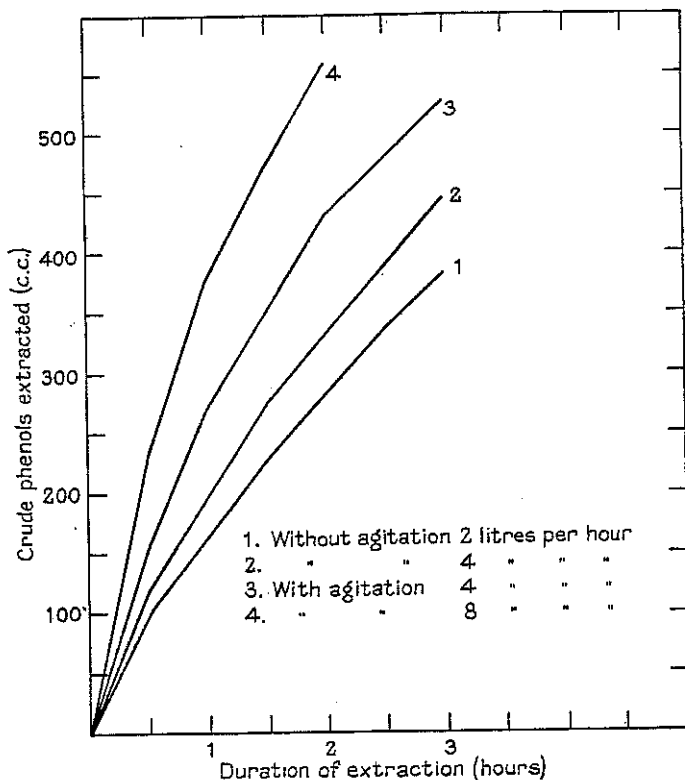


FIG. 54.

purposes a complete removal of the phenols from the oils will not be necessary. It will be sufficient to remove those tar acids which are corrosive or otherwise deleterious, that is to say, only those more readily soluble in water, since the corrosive acid properties depend upon their solubility in water.

*Experiments at Increased Rate of Pumping.*—We proceeded to experiment on the influence of an increased pumping rate on the efficacy of the extraction. Theoretically, it is to be presumed that the absorption of the phenols by the aqueous liquid will, with increasing water feed, more and more recede from

\* Only 3.5 litres of water were used in Expt. 1.

the saturation point. In this series of experiments the fraction 200–300° of the primary tar from Graf Bismarck Colliery was used. The experimental arrangements were the same as before at slower rates of pumping. In the first instance we worked with a rate of pumping of 4 litres per hour, without stirring; we then extracted 19 per cent. more phenols in the same time as before. Since the high rate of pumping might not leave the water in contact with the oil for a sufficiently long period, mixing of the liquid by stirring was tried. Thus the amount of phenols extracted was increased by about 4 per cent. when pumping at the rate of 4 litres per hour, compared with the experiment at 2 litres per hour without stirring. In a third experiment in which the rate of pumping was increased to 8 litres per hour, we extracted in two hours 560 c.c., against 280 c.c. in the first experiment at 2 litres per hour without stirring. The rate of extraction had therefore been doubled.

TABLE XXVIII

*Extraction Experiment with Fraction 200–300° from Primary Tar of Graf Bismarck Colliery.*

Duration of extraction.	Total crude phenols extracted.			
	1.	2.	3.	4.
	Without stirring.		With stirring.	
	Rate of pumping.			
	2 litres per hr.	4 litres per hr.	4 litres per hr.	8 litres per hr.
1 hr.	164	195	270	379
2 hrs.	280	335	433	560
3 hrs.	377	448	531	—

The curves of Fig. 54 will make these relations still clearer.

The phenol content of the extract did not vary noticeably in these four experiments; it ranged from 94 to 98 per cent. In Expt. 4, the heating gas had to be increased considerably owing to the high rate of pumping, in order to maintain a temperature at 225°. It was therefore of interest to inquire whether the phenol extraction could not be rendered more complete and rapid by raising the temperature. To decide this question in the easiest way an oil, which contained relatively little phenol and which yet had not been completely exhausted by treatment at 225°, was submitted to extraction.

*Extraction Experiment at 300°.*—Since the solubility in water of phenols increases with rising temperature, it was to be anticipated that the extraction

would become more efficient at higher temperatures. It was also to be expected that the phenol content of the extract would fall off markedly after a few operations. We had in particular to ascertain whether the proportion of hydrocarbons in the extracted crude phenols would rise with higher temperature. With a view to the industrial application of the process, it should be noted that a plant operating at higher temperatures would be more expensive and less safe on account of the increased pressure. At 225° the vapour pressure of liquid water is about 25 atm., a pressure which is not unusual in boiler practice; at 300° it is 85 atm. The question would therefore arise whether the advantages of operating at 300° would compensate for the difficulties which the construction and manipulation of the plant involve.

For this experiment we used a fuel oil from the primary brown coal tar of the Rositz works of the Deutsche Erdöl A.-G. We extracted the oil with water in the first instance four times at 225°, as in the previous experiments, and continued the extraction afterwards at 300°. Table XXIX shows the results.

In the first four extractions the quantity of crude phenols extracted dropped from 55 to 26 c.c. In the next extraction, at 300°, it rose to 100 c.c.; in the

TABLE XXIX

*Extraction of Fuel Oil from Rositz Brown Coal Primary Tar  
(boiling 180° to 310°) at 225° and 300°*

Extract No. . . .	Extracted at							Total phenols separated.
	225°.				300°.			
	1	2	3	4	5	6	7	
Phenols (c.c.) . .	55	45	34	26	100	108	56	424
Purity % . . .	about 95				55.5	47.5	36.5	

sixth, even to 108 c.c., but dropped off in the last to 56 c.c. There had thus been a very considerable increase in the quantity extracted. It is true that the phenols recovered at 300° showed an extraordinarily high percentage of hydrocarbons; this was indicated by the circumstance that the extracted phenols on separation from the aqueous solution did not sink to the bottom, but collected in a surface layer. The quantity of oil residue amounted to 950 c.c., and it contained only 3.3 per cent. of phenols.

These experiments, therefore, demonstrate that one can by the use of higher temperature reduce the phenol content to a greater degree than at

lower temperature, but that the products recovered are no longer pure phenols. The reason is probably that at 300° some of the hydrocarbons \* possess the same solubility as the least soluble phenols.

The mode of operation to be adopted in any particular case will therefore depend upon whether the purity of the hydrocarbons, or of the phenols, is the main object. On the whole, the latter will be preferable as an undue reduction of the oil residue is avoided, and because it is technically easier to work at the lower temperature and pressure.

In any case it can be asserted that the extraction of phenols with superheated water offers a means of reducing the phenol content of primary tar oils sufficiently for their utilisation as motor fuels, without the application of any chemicals and without the production of waste products or waste liquors. The extraction will further remove any products which are soluble in water, even to a slight extent, and there is therefore no question of a corrosive action of the refined tar oils on the metal of engines, even in the presence of moisture.

#### 4. *The Reduction of Phenols of Primary Coal Tar to Benzol and Toluol*

In the conclusion of the section on "The Utilisation of Phenols" it was pointed out that it would be of special value to convert the phenols of primary tar oils by chemical means into other more useful motor fuels. Two methods seem to be available for this purpose: hydrogenation and formation of the homologues of cyclohexanol, or the elimination of oxygen with formation of homologues of benzene. The former method is feasible with the use of catalysts. The method will hardly be adopted, as the oils would first have to be freed of sulphur compounds by means of metallic sodium, a course not feasible with phenols, nor practicable for economic reasons. Without this purification, the catalyst applied will be quickly poisoned and rendered ineffective.

The first mode of working can also be followed by dispensing with catalysts and making hydrogen react at temperatures of about 400° and at high pressure. Whether or not homologues of cyclohexanol can be produced in this way is not yet proved. In any case high pressures will be avoided as long as there is a method of effecting the conversion of the phenols into low-boiling hydrocarbons in other ways.

It is indeed possible to eliminate oxygen from phenols<sup>100</sup> by passing them, together with an excess of hydrogen, through iron pipes at a temperature of 750°. Ordinary iron pipes would not stand this treatment for any length of time, as they are rapidly burned through by the flame gases. There are, however, special kinds of cast iron which can be formed into resistant pipes. It is further possible to protect the external surface of common iron pipes

\* Whether this is a definite type of hydrocarbons remains to be seen.



by coating them with aluminium-bronze,<sup>101</sup> or by spraying-on aluminium, or by coating them by some process corresponding to sherardising.

Using such pipes, one soon notices that carbon is deposited, which after a time leads to clogging of the pipe. The yield of benzol and toluol is moreover very poor, evidently because part of the phenols, or part of the aromatic hydrocarbons already formed, is decomposed into carbon and hydrogen under the catalytic influence of the iron. Porcelain tubes being out of the question for works use, and fireclay pipes being too permeable to hydrogen, one seems to be tied down to the use of iron pipes. It has been found that catalytic action of the iron can be entirely suppressed by tinning the inside of the tube. The inner surface then turns, in the course of time, into a tin-iron alloy which no longer has the undesired property of iron itself to induce liberation of carbon catalytically. The iron forming a chemical compound with the tin no longer exists in the free state, and the tin-iron alloy is evidently unable to effect a catalytic deposition of carbon by a transient formation of carbide. Tin was selected for coating the inner walls of the tube because all tin compounds which might conceivably be formed would, under the experimental conditions, again be reduced by hydrogen to metallic tin at 750°, and because metallic tin is not volatile at that temperature. In the course of numerous experiments, it has been found that the protective action of the tin is maintained, provided the hydrogen used for the reduction of the phenols is pure. It is then possible to effect the conversion of phenols into benzene hydrocarbons without carbon deposition in an iron pipe, with a yield of almost 100 per cent. of the theoretical. If, however, the hydrogen is replaced by the cheaper water gas, the yields are much poorer and there is deposition of carbon in the reaction tube. This carbon might have been formed by the decomposition of carbon monoxide into carbon dioxide and carbon. But the reduction in the yield of aromatic hydrocarbons suggests that at least part of this carbon is derived from the decomposition of phenol or benzene homologues. On switching over from water gas to pure hydrogen, the disappointing observation is made that good yields are no longer obtained, and that there is deposition of carbon. The protective action of the tin has vanished, or has been reduced, obviously by some deleterious action of carbon monoxide upon the tin-iron alloy. On examining the interior of the pipe after removing the carbon dust, it is found that the tin-iron coating has peeled off in the form of a brittle, bright mass. This was observed in the case of the large tube which was used in the experiments to be described below, and it was feared that the inner surface of the iron, having apparently taken up a good deal of carbon, could not be retinned at all. Desiring to continue the experiments with the comparatively large tube already fitted up, the happy idea occurred to us to convert the inner surface of the pipe into iron sulphide.<sup>102</sup> It was to be supposed that the sulphur would inhibit the catalytic action of the iron, or iron carbides, on the deposition of

carbon. The conversion of the iron into sulphide at high temperature, by means of hydrogen sulphide diluted with nitrogen, did not offer any difficulties. There remained the question how long the sulphide coating would last, and whether, in the reduction of phenols by hydrogen, iron sulphide would not be reduced in the course of time and sulphur be carried away as hydrogen sulphide. Preliminary experiments on a small scale demonstrated that an ordinary gas pipe which, without previous treatment, gave poor yields and carbon deposits when phenol vapours and hydrogen were passed through it at 750°, immediately showed a yield of 90 per cent. without formation of carbon after having been sulphided on the inner surface. This protective coating of sulphide remained efficient throughout the whole series of experiments.

*Fundamental Experiments on a Small Scale* <sup>103, 104</sup>

It appeared useful to ascertain in the first instance what yields of benzene or toluene might be expected in the reduction of the individual phenols. Reduction in molecular weight may be produced not only by splitting off oxygen in the form of water, but also by a scission of the methyl group in the form of methane. In the case of cresol, for instance, the following reactions may occur :—

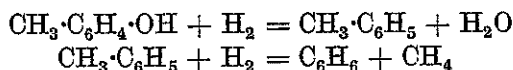


TABLE XXX

Yield from	Molecular Weight.	Xylene. %	Toluene. %	Benzene. %
Xylenol . . . . .	122	87	75	64
Cresol . . . . .	108	—	85	72
Carbolic acid . . . . .	94	—	—	83
Xylene . . . . .	106	—	87	74
Toluene . . . . .	92	—	—	85

The theoretically possible yields of xylene, toluene and benzene, starting from the different phenols, are summarised in Table XXX. Xylenol, it will be seen, can yield at the most 64 per cent. of benzene by splitting off two methyl groups in the form of methane and one atom of oxygen in the form of water. Conditions are somewhat more favourable with cresol, which gives a theoretical yield of 72 per cent. by weight. The table also gives the hydrocarbons xylene and toluene as raw materials for benzene. Xylene may yield 74 per cent. by weight of benzene; toluene, 85 per cent. From the theoretical yields mentioned in the following tables, the absolute yields may easily be calculated with the help of Table XXX.

TABLE XXXI  
*Suitability of different Phenols*

	Crude benzol.		Gas.	
	% of theory.	% of quant. used.		
Carbolic acid . . . . .	65	—	Coal gas	Tinned iron tube
<i>m</i> -Cresol . . . . .	99	—	H <sub>2</sub>	
Xylenol . . . . .	72	—	H <sub>2</sub>	
Primary tar phenols from :				
Bituminous coal 200–250° . . . .	—	66	H <sub>2</sub>	
"       "   250–340° . . . .	—	15	H <sub>2</sub>	
Brown coal 200–240° . . . .	—	50	H <sub>2</sub>	

How the different phenols behave when treated with hydrogen in the tin-coated iron tube is shown in Table XXXI. The figures are minimum values which might possibly be raised by the adoption of other temperatures or rates of flow. "Optimum" conditions were worked out for *m*-cresol, and all the other phenols were studied under the same conditions. The upper half of Table XXXI, which concerns definite chemical compounds, gives theoretical percentages; in the lower half, dealing with commercial mixtures, results are expressed in percentages of quantities used. It will be seen that the primary tar fractions 200–250°, which, by their boiling points, correspond to the cresols and xylenols, gave very favourable results whether obtained from bituminous or from brown coal. As Table XXX shows, xylenols can theoretically never yield more than 64 per cent. of benzene. The conversion of the low-temperature phenols, boiling between 200° and 250°, *i.e.*, the bulk of the phenols, into benzene, is therefore very promising. The higher-boiling phenols undoubtedly give a smaller yield of benzene. The actual yield of 15 per cent. represents about 25 to 32 per cent. of the theoretical, and modifications in the experimental conditions will possibly lead to improved results.

Table XXXII shows the behaviour of various hydrocarbons in the tinned iron tube at a temperature of 750°.

Only 7 per cent. of the hexane used is converted into benzene. This figure is quite in accord with older experiments of Haber,<sup>105</sup> and finds its explanation in that benzene is not formed from hexane by dehydrogenation and closure of the ring, but synthetically from the gases such as acetylene, liberated upon the decomposition of hexane. Similar considerations apply to the other petroleum products mentioned in Table XXXII, and also to the hydrocarbons of the primary tar from coal which in general resemble petroleum.

TABLE XXXII  
*Suitability of Hydrocarbons*

	Tinned iron tube with H <sub>2</sub> . Benzol at 750°
Aliphatic hydrocarbons.	
Hexane (benzine) . . . . .	7.2% of quantity used
Petroleum . . . . .	16.0% " " "
Wietze crude oil . . . . .	18.0% " " "
Primary tar hydrocarbons from bituminous coal 275-300° . . . . .	16.0% " " "
Aromatic hydrocarbons.	
Toluene . . . . .	100% of theory
Toluene and hexane . . . . .	47% of quantity used
Para-cymene . . . . .	74% of theory
Solvent naphtha I . . . . .	61% of quantity used
" " II . . . . .	44% " " "
Anthracene oil . . . . .	11% " " "
Diphenyl . . . . .	95% of theory
Naphthalene . . . . .	unaltered
Anthracene . . . . .	"

Table XXXIII gives some information concerning the influence of temperature in the use of the tinned iron tube. There is no reduction below 700°, but above 800° decomposition is considerable with formation of naphthalene. A temperature of 750° has so far been found the most favourable.

TABLE XXXIII  
*Influence of Temperature*

Tinned iron tube . . . . .	below 700°	Unchanged cresol.
10 times theoretical amount of hydrogen . . . . .	750°	Benzene and toluene.
o-Cresol . . . . .	above 800°	Decomposition with formation of naphthalene.

Another series of experiments was made to ascertain whether hydrogen is replaceable by other gases. Table XXXIV indicates that a mixture of carbon monoxide and hydrogen in equal proportions, *i.e.*, water gas, answers as well as hydrogen, if applied in large excess in an internally-glazed porcelain tube. Carbon monoxide, instead of hydrogen, gave only 47 per cent. of the theoretical yield. Even in the absence of reducing gases, working in an atmosphere of nitrogen, 41 per cent. of the theoretical yield of benzene was obtained. The explanation is probably that the decomposition of part of the cresol furnishes the hydrogen for the reduction of another part. Further experi-

ments were made with the tinned iron pipe, when 99 per cent. of the theoretical yield was obtained with hydrogen, and 75 per cent. with town's gas.

TABLE XXXIV  
*Influence of Kind of Gas*

Cresol at 750°.	
	Benzol % of theory.
In porcelain tube.	
H <sub>2</sub>	72
N <sub>2</sub>	41
CO	47
CO + H <sub>2</sub>	78
In tinned iron tube.	
H <sub>2</sub>	99
Coal gas	75

In the previous experiments in porcelain tubes we worked with a very large excess of hydrogen. It was of importance to ascertain how far this excess might be reduced, and how close the theoretical proportion of hydrogen could be approached. The practical importance of an approximately theoretical hydrogen requirement is that the benzene will separate spontaneously on cooling, and that only a small volume of gas need be washed for the complete recovery of the benzene. Although absorbents, such as activated carbon, are now available for the removal of the last traces of benzene, it is always advantageous to restrict the volume of gas to be submitted to this process. Table XXXV shows that 2 mols. of hydrogen are required per 1 mol. of cresol to convert it into benzene, methane and water. How closely that figure can be approached, without undesirable secondary reactions, will be seen from the fact that 99 per cent. of the theoretical yield of benzene is obtained using 10 mols. of H<sub>2</sub>, *i.e.*, 5 times, and 95 per cent. with 3 mols. of H<sub>2</sub>, *i.e.*, 1.5 times the theory.

TABLE XXXV

*Influence of Quantity of Hydrogen for m-Cresol in Tinned Iron Tube, at 750°*

Theory requires 2 mols. H <sub>2</sub> for			
$\text{CH}_3\text{C}_6\text{H}_4\text{OH} + 2\text{H}_2 = \text{C}_6\text{H}_6 + \text{CH}_4 + \text{H}_2\text{O}.$			
10 mols. H <sub>2</sub>	.	.	99% benzene
3    "   "	.	.	95%    "

The aromatic hydrocarbons behave somewhat differently, and are still more readily converted into benzene. Toluene can be converted with a

theoretical yield of 100 per cent. A mixture of equal parts of toluene and hexane yields 47 per cent., as much as can be expected, and *p*-xylene gives 74 per cent. A good yield is also obtained from the two solvent naphthas.

Whilst diphenyl combines with 1 mol. of hydrogen giving the theoretical yield of 92 per cent. of benzene, the yield from anthracene oil is very small; naphthalene and anthracene are not converted at all under these conditions. Table XXXVI shows the suitability of various low-temperature tar oils, that is, fractions of primary tar which contain hydrocarbons as well as phenols and small quantities of bases.

For the reasons stated the yields are given in percentages of the material used. The fractions boiling between 200° and 250° are again seen to give the best results.

TABLE XXXVI  
*Suitability of Primary Tar Oils*

	Crude benzol % of quantity used.	Gas.	Tube.
Primary tar oils, below 305° . . . . .	20	H <sub>2</sub>	Tinned Fe Porcelain tinned nails
„ „ (bituminous coal) 250–270° . . . . .	15	H <sub>2</sub>	
Middle oil (coke-oven tar) (29% phenols) . . . . .	45	H <sub>2</sub>	Tinned Fe
Brown coal primary tar . . . . .	29	H <sub>2</sub>	
Primary tar oils (bituminous coal) 200–250° (50% phenols) . . . . .	40	H <sub>2</sub>	
Primary tar oil (bituminous coal) 250–300° (40% phenols) . . . . .	30	H <sub>2</sub>	

The treatment of the whole tar with hydrogen at 750° in the tinned iron tube for the benzol recovery may, under certain conditions, be advisable. In that case the low-boiling constituents of the tar should be distilled off in the first instance.

Table XXXVII gives an indication of the relative stability of the benzene homologues with respect to the scission of methane.

TABLE XXXVII  
*Stability of Benzene Homologues at 650°*

Reduced to benzene with CH<sub>4</sub>-formation.

Cymene . . . . . almost completely.  
Xylene . . . . . partly.  
Toluene . . . . . hardly.

Cresol forms at 700° benzene and some carboic acid.

Methane is split off at 650°, the easier the higher the methylation of the material.

So far a reduction to benzene only has been discussed. In reality some toluene will always be present. Table XXXVIII shows that in general a mixture of approximately 5 parts of benzene and 1 part of toluene will result, which as a motor fuel is superior to pure benzene, on account of the liability of the latter to crystallise in the cold. The term benzol here designates all those products boiling between 80° and 95°; toluol, those boiling between 95° and 115°.

TABLE XXXVIII  
*Ratio of Benzene to Toluene*

From cresol . . . . .	15.5 : 2.7	} 5 parts benzene to 1 part toluene.
„ primary tar phenols .	15.6 : 3.4	

Fraction 80–95° calculated as benzene, 95–115° as toluene.

*Experiments on the Large Scale* <sup>106</sup>

On the strength of these preliminary experiments, the following experiments, on a larger scale, were carried out in the apparatus illustrated in Figs. 55 and 58.

The apparatus consists of three main portions :

- (1) Vaporiser and oil feed.
- (2) Tinned iron tube and furnace.
- (3) Condensers.

(1) *Vaporiser and Oil Feed*.—In the vaporiser, Fig. 55, the material to be reduced is converted into vapour and at the same time mixed with the reducing gas. It consisted of an iron cylinder, 5 mm. thick, tapering at both ends. One end was closed by a screw-cap to make the interior accessible for cleaning. The other end was welded to a tube which could be connected by means of a union to a short pipe projecting from the cover of the large reduction tube. A thermometer pocket was provided for temperature readings in the middle of the cylinder. As shown in Fig. 55, two inlet tubes passed into the vaporiser vertically from above; one for the oil vapour, the other obliquely, for the gas. The latter was bent so as to set up turbulence in the cylinder for the intimate mixture of the oil vapours with the gas. A glass funnel was cemented with talcum and silicate of soda into the vertical oil feed pipe, by means of which the rate of flow of the phenols could be observed. The vaporiser was heated by a row of high-pressure burners. The cylinder was provided for a length of about 30 mm. with an asbestos-lined sheet-iron jacket, in which a number of holes were drilled for the ready escape

of the gases. A feed bottle, provided with a syphon pipe closed by a full-bore stop-cock, was mounted about 1.5 metres above the vaporiser. The lower end of the pipe was attached by means of india-rubber tubing to a capillary syphon which was fixed into the glass funnel with the aid of a rubber stopper. The bore of the capillary was chosen according to the desired rate of oil feed; the feed-bottle had a constant-pressure device so as to maintain an even oil feed.

(2) *The Tinned Iron Pipe.*

—The iron tube was 3 metres long, 28 cm. internal diameter, and had a wall thickness of 10 mm. The inner surfaces of the tube and cover were tinned by a competent firm. The coating was bright and apparently very uniform. The covers were flanged and bolted to both ends of the pipe. The cover nearest the vaporiser was provided with a safety-valve, made by cutting into it a hole of 18 cm. diameter, over which an iron plate with projecting edge was ground. This plate was pressed against the cover by a spring held by a strap.

The joint was kept gas-tight by means of oil and graphite. The reaction tube rested on a frame of angle iron, forming two supports which also carried the fire-clay shapes surrounding the reaction tube. One of these

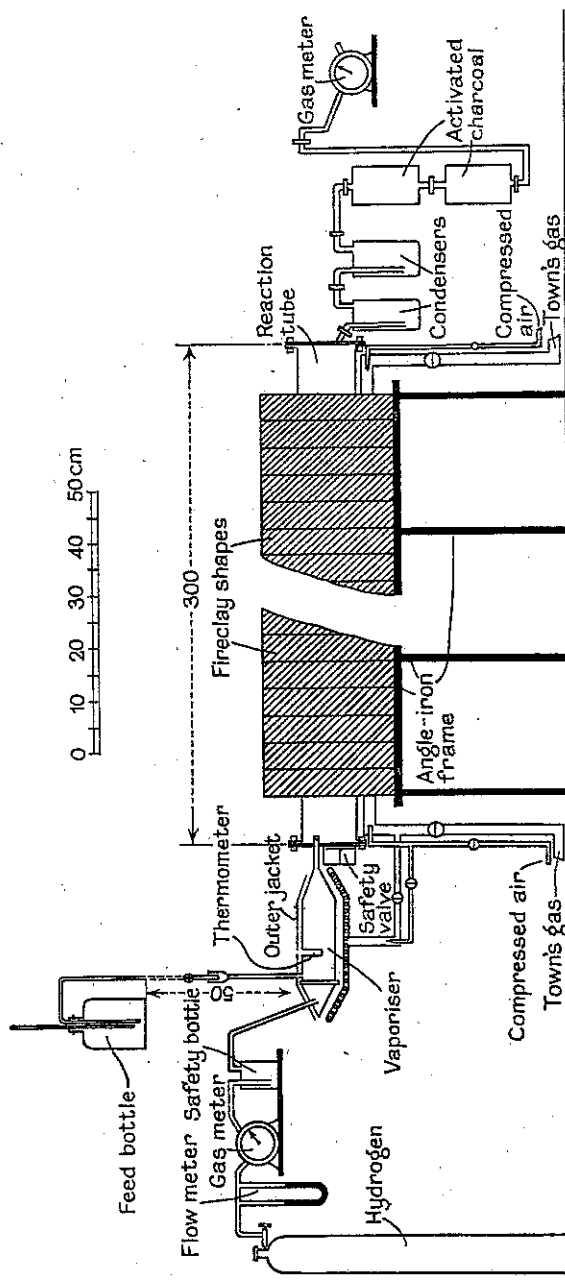


FIG. 56.



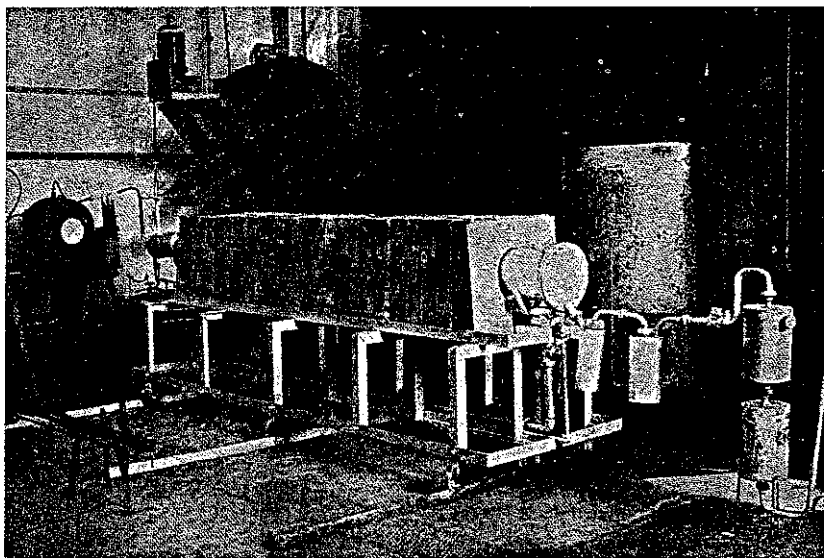


FIG. 56.

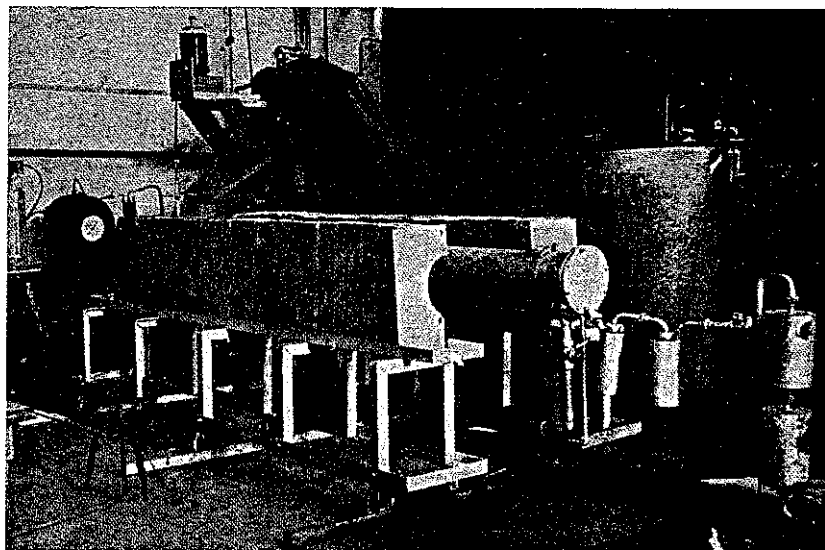


FIG. 57.

supports was mounted on wheels, so that the tube was easily accessible (Figs. 56 and 57). In order to ensure a uniform distribution of heat, two independent sets of gas burners were used, each row heating half the length of the reaction tube, and being controlled by gas and compressed-air

taps fixed at the ends of the frame. The burner pipes had a diameter of  $1\frac{3}{4}$  inches, and were provided with three rows of staggered holes, 3 mm. diameter, 10 cm. centres. Fig. 58 illustrates the shape and dimensions of the fire-bricks. They were held in position on the angle iron frame by iron wire. The reaction tube projected from the bricks at each end by about 40 cm. In order to prevent its destruction by oxidation, the tube was given a coat of aluminium-bronze.<sup>101</sup> This behaved very satisfactorily, and throughout the series of experiments conducted at temperatures between  $700^{\circ}$  and  $800^{\circ}$  the tube was hardly attacked.

(3) *Condensers*.—The right end cover of the tube carried a tube inclining downward, which was joined to the condensers by a union. The condensers consisted of two sheet-iron pots for the reception of the liquid condensate, and two cylindrical drums to be charged with activated carbon. The first condenser was cooled by means of water, to retain the less volatile products; the other by a freezing mixture of ice and salt, to condense the more volatile constituents.

The gases leaving the second condenser were passed through the two absorbers charged with activated carbon, for the extraction of benzol vapours. The gases were then passed through a gas meter and burned. The internal arrangements of the drums, shown in Figs. 56 and 57, were the same as in the

large drums to be mentioned below, but the wire gauze and feed-pipe in the middle were dispensed with. The end of the gas intake pipe, which reached a few centimetres into the drum, was closed by a plate, but provided with a ring of lateral perforations which distributed the gas uniformly over the whole surface of the drum. The carbon was placed between nets of wire gauze. Openings, closed with caps, were provided at the sides for charging the drums with the charcoal. The different parts of the condensers were assembled with screw connections.

This condensing arrangement was inadequate for experiments at high rates of flow, and a larger plant was installed. It had in the place of the two condensers a water-cooled coil with receiver, to which the two large drums charged with activated carbon were joined.

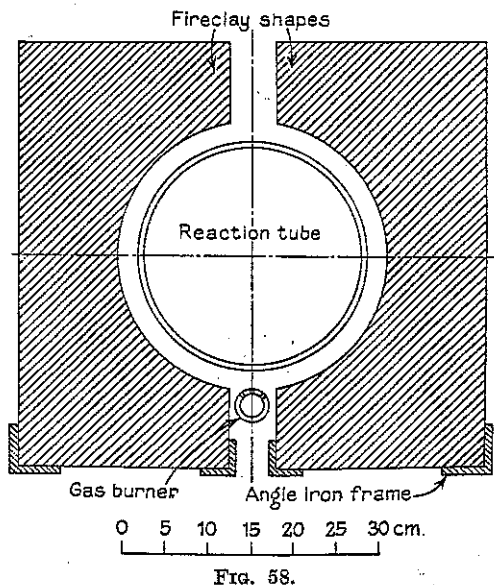


FIG. 58.

*Experimental Data.*

The gas used in the reaction, which was generally taken from a steel cylinder, passed through a flow meter and a gas meter, as shown in Fig. 55.

The experiments were conducted in the following way :—

All the air having been expelled from the apparatus by means of coal gas, the apparatus was tested for leaks with a flame. The tinned iron tube was then heated to 750°, while the coal gas was kept flowing. The temperature had to be raised very slowly, since the lower side of the pipe would heat up quicker than the upper, thus causing bending of the long tube owing to the expansion of the lower side, and possibly fracture of the fire-bricks. Temperatures were continuously observed by means of a Wanner pyrometer directed on the upper portion of the tube through the opening between the fire-bricks. When the temperature had remained constant for some time, the current of coal gas was replaced by the reaction gas. The vaporiser had meanwhile been heated up and the oil feed tap was opened. After the completion of the experiment the oil tap was closed, and the gas meter was read. A little more gas was passed through the tube in order to expel the reaction products from it. The amount of phenol oil used was ascertained by weighing the feed-bottle before and after the experiment, and the increase in weight of the condensers was also determined. The working-up of the oil condensed in the first two vessels will be explained below. Besides ascertaining the increase in weight of the carbon filters, in most cases we expelled the benzol absorbed, by means of superheated steam. For this purpose it proved necessary to raise the temperature at the outlet of the charcoal drum to 250°. This steaming took two hours from cold, and finally a slow current of air was passed through the drum to displace the water vapour. The results obtained with this apparatus will be described subsequently, but it may be mentioned here that the throughput of our tube was as much as 12 kg. per hour, or about 300 kg. of oil in 24 hours. For larger capacities the diameter of the tubes could be increased, or a number of them could be arranged as in a setting of horizontal gas retorts. Further experience might also suggest the advisability of a vertical reaction tube. With this outfit the following experiments were conducted.<sup>107</sup>

*Experiment 1.*—In Experiment 1 with cresol, the rate of drip was so adjusted that the throughput amounted to only 200 grams per hour. The rate of hydrogen feed was set to 1½ times the theoretical. We obtained 90 per cent. of the theoretical yield of crude benzol. Apart from small leaks, which were easily stopped, the apparatus proved perfectly satisfactory. No carbon was deposited in the reaction tube.

*Experiments 2 and 3.*—We then directed our attention to the material which claimed it first and foremost, viz. the phenols from primary tar. In Experiments 2 and 3 the drip rate was adjusted so that from 200 to 300 grams

of substance passed through the tube per hour. The raw material of Experiment 2 was the primary tar phenols from Röchling producer tar, fraction 150–250°, prepared by extraction with water under pressure as described on p. 110. The phenols had been redistilled after extraction and boiled between 190° and 250°. In Experiment 3 we used phenols likewise prepared from crude producer tar by extraction with water and therefore representing a mixture of primary tar phenols of higher and lower boiling points. To render the experiments more simple with a view to subsequent technical application, the phenols were not redistilled, but used as obtained by extraction and mechanical separation. The quantity of material, 441 grams, available for Experiment 2, was rather small for the large apparatus. In order to ascertain the conditions for maximum yields, we worked with  $2\frac{1}{2}$  times the theoretical amount of hydrogen. The total yield of crude benzol, which consisted of 205 grams of benzene, 48 grams of toluene, and 5 grams of xylene, amounted to 58.5 per cent. of the quantity used. Allowing for minor leakages in this experiment, one may reckon upon an average yield of 60 per cent. Assuming that the phenols from primary tar consist of cresols and xylenols, which by scission of the hydroxyl groups and side-chains form  $H_2O$  and  $CH_4$  and could give only 64 to 68 per cent. of benzol, the yield obtained must be considered very satisfactory. Unchanged phenols were not found in the condensate. Small quantities of solid hydrocarbons, chiefly naphthalene, were found in the distillate even at lower temperature; above 180°, the distillates congealed completely. Higher-boiling constituents continued to come over up to and beyond 360°. They consisted mainly of naphthalene, and probably of higher aromatic hydrocarbons, such as had always been observed in small-scale laboratory experiments. In Experiment 3 the yield of benzol, which consisted of 315 grams of benzene, 41.5 grams of toluene, and 7 grams of xylene, dropped to 39.6 per cent. This was to be expected, since we had started from a mixture of higher and lower boiling phenols and, according to our preliminary experiments, the higher phenols give only a low yield of benzene (about 15 per cent.) by thermal reduction with hydrogen. This experience was confirmed by Experiment 4 in the large apparatus. The yield of Experiment 3 may therefore also be considered relatively satisfactory.

*Experiment 4.*—This experiment, particulars of which are given in Table XXXIX, was made in order to ascertain whether the higher-boiling phenols from primary tar, 210–270°, would give better benzol yields when operating on a larger scale. Having meanwhile ascertained by Experiments 5 to 9 that the experiments may be performed at a much accelerated rate of feed of the phenols to be reduced, without detriment to the benzol yield, we raised the input to 4 kg. per hour and kept the hydrogen supply at an excess of about  $1\frac{1}{2}$  mols. of the theory, taking the average molecular weight of the phenols as 100, which is probably too low. The yield obtained was 33.3 per cent. of the amount used. The

experiment therefore indicated, in confirmation of our previous experience, that the phenols boiling above  $250^{\circ}$  give a much lower yield in benzol than those of lower boiling point. For the fairly good results of Experiment 4, dealing with fraction  $210\text{--}270^{\circ}$ , credit must be given to that portion boiling below  $250^{\circ}$ .

The result of the last three experiments on a large scale confirms the small-scale experience, that the phenols of primary tar boiling below  $250^{\circ}$  may be reduced, like cresols, by means of hydrogen at high temperature with good yields. With the higher-boiling phenols the yields drop off considerably.

*Experiments 5 to 9.*—Experiments 5 to 9 were undertaken for the purpose of ascertaining how far the capacity of the apparatus could be increased. They were made with a commercial cresol mixture. The rate of feed was doubled at the end of each hour, 99 litres of hydrogen being finally passed through the tube per minute. The original absorption apparatus could not deal with such large volumes of gas, and was replaced by the larger apparatus already mentioned.<sup>105</sup> Owing to the strong cooling action of the gas, and in order to increase the velocity of reaction between phenols and hydrogen, it proved necessary to raise the temperature of the tube to  $800^{\circ}$ , lest a considerable portion of unreduced phenols should be found in the condensate.

Even the enlarged apparatus did not prove quite sufficient for the last experiments, Nos. 7, 8 and 9, and a quantitative collection of the benzol was dispensed with. We contented ourselves with the estimation of unreduced material in the condensates, as a measure of the extent of phenol reduction. Table XXXIX shows that the proportion of unreduced raw material increased with the higher throughput. With a throughput of 12.3 kg. per hour, this proportion amounted to 16.2 per cent. It was higher in Experiment 8, where the temperature was too low. The experiments prove at any rate that a plant of the size of ours will, with proper temperature control, convert about 12 kg. of cresol per hour into benzol with a good yield.

*Experiment 10.*—Experiment 10 of Table XXXIX was made in order to see whether hydrogen might be replaced by a cheaper gas, such as coal gas. The coal gas at our disposal was a coke-oven gas containing about 50 per cent. of hydrogen. The available gas supply not being sufficient for our rates of feed, the gas was compressed in a steel cylinder to 150 atm. The gas rate was regulated in such a way that, considering that half of the coal gas consisted of hydrogen, we had about  $2\frac{1}{2}$  mols. of hydrogen at our disposal. Table XXXIX shows that we limited the throughput to less than 1 kg. of cresol per hour, so as to allow for the increased gas volume to be dealt with by the absorption train. The benzol yield was 73 per cent. of the theoretical, *i.e.*, 17 per cent. less than in Experiment 1 with hydrogen. This diminution was evidently connected with the deposition of a little soot on the tin-coated iron, the cause

TABLE XXXIX

*Reduction of Cresols and Primary Tar Phenols with Hydrogen or Coal Gas at 750–800° in the large Apparatus*

No.	Substance used.		Gas.		Condensates.						Condensates contain.				Remarks.			
	Kind.	Amount. g.	Through-put per hour. g.	1 mol. subst. in mol. gas.	Rate per min.	Receiver.			Act. charcoal.			Crude benzol 80-180°.				Un- decomp. raw material. %	Hydro- carbons boiling above 180°. g.	
						I.	II.	g.	I.	II.	g.	Total.	Total.	% of theory.				% of quantity used.

Experiments with hydrogen.																	
1	Tri-cresol.	510	219	3.4	12	103	115	214	23	—	—	455	330	90.0	64.7	—	—
2	Primary tar phenols 190-250°	441	220	4.25*	14.5	103.1	15.5	170.5	77.5	—	—	366.6	258	—	58.5	—	*100 g. substance in mol. gas.
3	Phenols from total primary tar.	919	290	5.2*	—	161	219.3	296.3	38.5	—	—	715.1	363.5	—	39.6	—	208.5
4	Primary tar phenols 210-270°.	945.5	3,790	3.7*	21	108.9	113	55.3	292	10	—	579.2	315	—	33.3	—	200
5	Tri-cresol	1,075	815	2.25	8	241.5	103	253	0.5	—	—	598	395	50.9	36.7	—	135
6	"	890	1,330	4.45	36	192	101	283	9	—	—	585	402	62.5	45.2	0.4	110
7	"	886.5	3,100	2.83	37.3	72	99	294	121	21	—	607	523	81.7	59.0	0.6	48
8	"	2,088.4	8,300	2.95	75	782	—	588	300	—	—	1,670	—	—	—	18.7	391
9	"	2,475	12,300	2.77	99	950	—	508	402	—	—	1,860	—	—	—	16.2	550
Experiments with coal gas.																	
10	"	330	890	6.4	16	41.2	31.1	128.4	40.6	—	—	241.3	174	73.0	52.7	—	40

Benzol yield inaccurate through inadequate absorption.																	
Slight separation of soot.																	

Slight separation of soot.

Benzol yield inaccurate through inadequate absorption.

See remark to 6-9.

TABLE  
*Reduction of Tri-cresol and Brown Coal Creosote*

No.	Substance used.			Gas.		Condensates.					
	Kind.	Amount. g.	Throughput per hour. g.	1 mol. subst. contained in mol. gas. g.	Rate per min. g.	Receiver.		Charcoal.			Total. g.
						I.	II.	I.	II.	III.	
						g.	g.	g.	g.	g.	g.
1	Tri-cresol . . .	1843	3000	2½	23.5	360	—	400	470	—	1230
2	" . . .	2719	3000	2½	23.5	275	701	500	400	—	1876
3	Brown coal creosote	2082	2000	—	19	134	267	650	300	—	1351
4	" " "	1883.5	2000	—	19	120	250	600	450	—	1420
5	" " "	1620.1	2000	—	19	30	75	480	310	—	895

of which could not be ascertained definitely, although the decomposition of the ethylene and similar constituents of coal gas was suspected. Another explanation is that iron carbonyl, which is present in gas containing carbon monoxide, particularly after compression in steel cylinders, upon decomposition at high temperature into metallic iron, catalytically induces the deposition of carbon.

It has already been mentioned that water gas when used instead of hydrogen spoiled the iron tube. The following Experiments, 3 to 5, Table XL, were made<sup>102</sup> with the tube after revivification by sulphiding, with a brown coal creosote placed at our disposal by the Deutsche Erdöl A.-G. The creosotes, practically free of neutral oils, were first distilled down to pitch to remove the high-boiling constituents which are of little use for this reaction. Thirty-one per cent. of pitch was left on distilling the creosote from 200° to 240°. The experiments were made with hydrogen and a throughput of 2 kg. of creosote per hour. Assuming that the creosote consisted mainly of xlenols, the hydrogen rate was adjusted on the basis of an excess of ¼ mol. over the theoretical requirement. Table XL shows that the yield was about 40 per cent. of the quantity used, in agreement with the results of previous experiments. The benzol was brown in colour, smelled of pyridine and had a specific gravity of 0.89. Distilled by Spilker's method, it gave the fractions :

Below 85° . . . . .	68 per cent.
85-95° . . . . .	18 "
95-113° . . . . .	3 "

The product then consisted largely of benzene, with very small pro-

XL

with Hydrogen at 750–780° in the large Apparatus

Condensates contain					Gas analysis.						Calorific value of reaction gas.
Crude benzol 80-180°.			Undecomp. raw material.	Hydrocarbons boiling above 180°.	CO <sub>2</sub> .	O <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	Unsat. hydro-carbon.	
Total.	% of theory.	% of quantity used.									
g.			%.	%.	%.	%.	%.	%.	%.	%.	Cals.
1090	81.9	59	—	not det.	0.4	0.8	12	58.8	19.6	—	3412
1510	76.9	55.5	—	„	—	—	—	—	—	—	—
855	—	41	—	„	0.6	0.8	17.8	46.8	23.2	—	3876
790	—	41.8	—	„	—	0.2	15.6	50.2	20.8	0.6	—
630	—	38.8	—	„	—	0.2	13.2	54.0	23.4	1.2	3794

portions of higher homologues. It should be mentioned that a high cresol velocity favours the formation of toluene, whilst at a slower rate benzene predominates. This observation is explained by the fact that for a complete removal of the methyl group the molecules must be kept at high temperature for prolonged periods.

It should, therefore, be possible to obtain in commercial working a product richer or poorer in toluol by modifying the mode of procedure. We had to content ourselves with a slow throughput of creosote in order to be able to absorb the benzol quantitatively in our condensation plant. In working-up the reaction products of all the experiments of which details are given in Table XL, we proceeded in the manner already described.<sup>107</sup> The figures given for benzol in the table apply to crude benzol obtained by steaming the activated carbon of the absorption drum and "topping" the products collected in the receivers.

A few experiments were made with the object of replacing the reducing action of hydrogen by that of coke. This had not been attempted before, as it was feared that the mineral constituents, and particularly iron compounds, would induce deposition of soot. Since the favourable influence of sulphur had been established, it seemed promising, by a sulphiding treatment, to make the impurities in coke innocuous.

For this purpose semi-coke was treated in our iron tube by passing hydrogen sulphide over it for 3 hours at a red heat. "Tri-cresol" vapour was then passed through the tube together with a very gentle current of hydrogen sulphide. The benzol yield was 30 per cent. of the "tri-cresol" used. No soot was definitely found on the semi-coke at the end of the experiment. A



second experiment conducted in the same way, but with the addition of steam, gave an appreciable improvement in the yield. In this experiment again a deposition of soot could not be established with certainty. Owing to the low pressure of the town's gas mains at the time, the temperature of the experiment did not exceed  $700^{\circ}$ .

The object of some final experiments was to ascertain whether the reaction could be appreciably accelerated by enlarging the contact surface. The absorption capacity of our large apparatus being inadequate for these experiments, we had to proceed on a small scale in the following manner. We passed vapour of "tri-cresol" mixed with  $2\frac{1}{2}$  mols. of hydrogen per mol. of cresol through the sulphided pipe, only half the length of which was heated to  $750^{\circ}$ , at a velocity which exceeded the capacity of the apparatus, so that 20 per cent. of undecomposed cresol was condensed along with benzol and other reaction products. We then charged the pipe with sulphided iron turnings which approximately doubled the contact surface, and passed an equal amount of cresol vapour through the pipe under the same conditions. In this experiment only 13 per cent. of undecomposed raw material was collected in the receivers. A comparison of the proportions of unreduced cresols obtained in the first experiments shows,<sup>108</sup> in confirmation of previous results, that, by increasing the contact surface, the reaction velocity and the capacity of the reaction tube had been raised by one-third only. The observation justifies the supposition that the reaction is not influenced catalytically, but is entirely due to thermal decomposition.

Having noticed a smell of butadiene when steaming out the activated carbon, we investigated whether di-olefine hydrocarbons were formed by thermal reduction. In preliminary experiments we attempted to ascertain in the crude benzol the proportion of constituents boiling below  $70^{\circ}$ . For this purpose we fractionated 200 c.c. of benzol in a Dufton<sup>109</sup> spiral column, and obtained 2.1 c.c. of compounds which smelled strongly of isoprene and absorbed bromine readily. These figures are not final; further investigation of this problem and an exact estimation had to be postponed, since only part of the reaction products could be condensed in our apparatus.

To sum up: it has been demonstrated that a thin coating of iron sulphide protects the iron reaction tube, heated to  $750^{\circ}$ , during the thermal reduction of phenols to benzol, from the deposition of soot as effectively as a tin coating. No deleterious influence of the iron sulphide upon the reaction was noticed. A series of experiments with "tri-cresol" and with brown coal creosote gave yields in the sulphided tube as favourable as those obtained in a tinned tube. Coke which, owing to its ferruginous mineral constituents, deposits soot, lost this property after having been sulphided for several hours. Phenols may be reduced to benzol by sulphided semi-coke in a gentle current of hydrogen sulphide, with a yield of 30 per cent. The yield is increased to 40 per cent. by

the addition of steam to the mixture. Doubling the contact surface of the reaction tube raises the reaction velocity by one-third.

*Benzol by Reduction of Brown Coal Primary Tar Phenols*

The same apparatus served, while the internal tin coating was still intact, for experiments in which the preparation of benzene and its homologues from creosote of brown coal primary tar, was investigated. Numerous preliminary experiments on a small scale having proved quite satisfactory, they were tried on a larger scale.<sup>107</sup>

The raw material was a new consignment of technical brown coal creosote from the Deutsche Erdöl A.-G. The material was first distilled down to pitch in an iron pot, the oil boiling from 180° to 240°. Higher distillates were not obtained. The pitch residue amounted to about 20 per cent.; the water in the distillate to 3.4 per cent. The distilled oils were completely soluble in caustic soda, and, therefore, were free from neutral constituents. According to information supplied by the Works, this creosote had been extracted by caustic soda.

TABLE XLI

*Reduction of Brown Coal Creosote with Hydrogen and Coal Gas at 750–780° in the large Apparatus*

No.	Oil used.		Gas.		Condensates.						Condensates contain		
	Amount.	Through-put per hour.	100 g. oil contd. in mol. gas.	Rate per Min.	Receiver.		Act. Charcoal.			Total.	Crude benzol 80–180°.		Hydrocarbons boiling above 180°.
					I.	II.	I.	II.	III.		Total.	% of quant. used.	
	g.	g.		l.	g.	g.	g.	g.	g.	g.	g.		g.

Experiment with Hydrogen.

1 | 1299 | 3890 | 2.7 | 21 | 159.9 | 178.8 | 401.5 | 80.8 | 34 | 855 | 612 | 47.1 | 210

Experiment with Coal gas.

2 | 975 | 1950 | 7 | 21 | 111.8 | 107.3 | 329.7 | 66.1 | 15.0 | 630.1 | 390 | 40 | 60

The first experiment was made in a current of hydrogen; the second in a current of coal gas. In Experiment 1 an excess of hydrogen of  $\frac{1}{2}$  mol. was used, and the creosote feed was adjusted to a throughput of about 4 kg. per hour. The furnace temperature was kept between 760° and 780°. 47.1 per cent. of crude benzol boiling from 80° to 180° was obtained as calculated on the material used; the benzol produced was of a light yellow colour and smelled strongly of pyridine.

These experiments confirmed the results previously obtained on a smaller scale. Brown coal phenols may be reduced with hydrogen to benzene and small quantities of other hydrocarbons boiling below  $180^{\circ}$ , up to 50 per cent. of the original weight. In terms of calorific value, the yield is considerably higher, for the oxygen of the phenols has no calorific value. For example, 1 kg. of benzene has a calorific value of about 10,000 cals., 1 kg. of phenol  $C_6H_5 \cdot OH$  a value of about 7800 cals.; 78 kg. of benzene are therefore equivalent in calories to 100 kg. of phenol.

The light spirits formerly available, *i.e.*, benzol in aromatic coal tar and benzine from brown coal, have had benzine from bituminous coal added to their number in recent years. We have now established the conditions under which benzol may be produced from brown coal.

The benzine from the distillates of bituminous coal,\* brown coal and peat is a decomposition product of bitumen; some benzine exists preformed in coal. Benzol may be obtained from these fuels by our process of reducing the phenol of primary tar. The phenols themselves are not derived from bitumen, but from the ulmic constituents of coal. Benzol recovery from the gas and the ordinary tar of high-temperature carbonisation of bituminous coal, as practised in coke-ovens and gas retorts, is possible because, under the conditions prevailing there, primary phenols are reduced.

#### *Production of Hydrogen by the Diffusion Process.*

After it had been shown that phenols could be extracted from primary tar oil by means of superheated water, and reduced by extremely simple methods with hydrogen to benzene and toluene (which, it should be noted, is free from thiophene), it remained to find a cheap process for the supply of the requisite hydrogen. To replace hydrogen by coal gas or water gas did not prove feasible. It was found that hydrogen could be obtained from producer gas or water gas by a process of diffusion.

Producer gas will be available where primary tar is made in generators, or could be made from the semi-coke of low-temperature carbonising plant in sufficient quantity. There is no need to separate all hydrogen from a producer gas: it is quite sufficient to extract a few per cent. of hydrogen as long as this is of high concentration and contains as little carbon monoxide as possible.

In the case of a plant gasifying lignite briquettes in generators, 1 ton of briquettes would produce 100 kg. of tar containing 20 per cent. of phenol, say 20 kg. of phenol. Of these only one-half, *i.e.*, 10 kg., can be reduced. Let us assume a yield of 3000 cb. m. of producer gas per ton of briquettes, containing a total of 450 cb. m. of hydrogen. For reduction and demethylation to benzol, 10 kg. of cresols require about 4 cb. m. of hydrogen at the rate of 44.8 litres per gram-mol. of cresol (*i.e.*, 108 grams), this being 1 mol.  $H_2$  for reduction and 1 mol.

\* This is only partly true in the case of bituminous coal. Vide section "Extraction."

H<sub>2</sub> for demethylation. With a plant of this capacity the reduction of the phenol made could therefore be brought about by separating one-hundredth of the total hydrogen in the gas. This would mean practically no diminution in the calorific value of the producer gas.

The possibility of such a recovery of hydrogen has been discussed by Fischer, Schrader and Jaeger.<sup>110</sup> Fig. 59 explains the principle of the method.

In a welded sheet-iron vessel small contact rings of the Raschig or Lessing type are disposed on a grid of wire netting to a depth of 10 to 20 cm. Producer gas flows through the space below the grid whilst superheated steam passes over the contact rings in the opposite direction and with a slight positive pressure against the producer gas, the pressure being indicated by the gauge. The whole apparatus must be kept at 150° and well lagged so as to avoid condensation of steam.

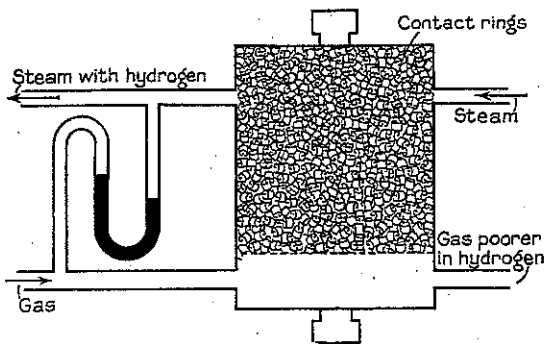


FIG. 59.

After condensation of the steam, hydrogen of high concentration can be obtained, even from gases of low hydrogen content.

#### 5. Benzine by Destructive Distillation of Primary Tar from Bituminous or Brown Coal

It has already been shown in the section on "Chemical Changes on Distillation" that distillation under ordinary conditions and at atmospheric pressure leads to considerable chemical changes in primary tars, particularly in the high-boiling fractions. Broadly speaking, there are two ways of causing a scission of hydrocarbons of high molecular weight into lighter products by the action of heat at atmosphere pressure. The products are either vaporised and the vapours brought into contact with surfaces of considerably higher temperature, in which case there is a fairly wide margin of temperature; or else the hydrocarbons are submitted to a very protracted distillation, when decomposition takes place at a temperature at or below, and certainly not appreciably above, the boiling point of the product. The experimental conditions may be varied and modified in many ways. At higher temperature the reaction will proceed more rapidly and violently; at a lower temperature, more time is required to carry scission to the same extent. The temperature also influences the yield and properties of the products obtained.

Protracted destructive distillation of primary tars proceeds similarly to that of petroleum. It affects chiefly the constituents boiling above 300°.

*i.e.*, viscous oils, paraffin wax and part of the high-boiling phenolic bodies.

It is well known that in the distillation at atmospheric pressure of oil mixtures, such as crude petroleum, more or less decomposition takes place according to the experimental conditions as soon as higher temperatures are reached. The higher fractions then do not consist of compounds which were originally present in the raw material, but of products derived from them by certain chemical changes. The temperatures at which decomposition sets in vary with the kind of crude oils; they lie, according to Engler,<sup>111</sup> between 200° and 250°. If the high-boiling constituents are to be obtained undecomposed, preserving conditions must be employed above these temperatures, such as distillation in a vacuum or in a current of superheated steam, or a combination of these two methods, a procedure which is practised in the manufacture of the lubricating oils from crude petroleum.

The break-down of compounds of high molecular weight into compounds of lower molecular weight may, on the other hand, be utilised for the purpose of enriching the lower fractions at the expense of the higher-boiling fractions, a practice originally introduced into petroleum refineries to secure higher yields of lamp oils.

A technical brown coal tar of the Riebeck Montan Works was subjected to destructive distillation.<sup>112</sup> This was not a true primary tar, but the results obtained will hold good for it, since previous work had shown that the distillation of primary tar conducted in the usual way yields products of the consistency and the general properties of commercial brown coal tar.

The experiments discussed in the following lines were made to clear up two points. In the first instance, the yield and properties, particularly of the light products, obtainable by slow distillation down to coke, were to be ascertained. Secondly, it was of interest to know whether and to what extent by such cracking, if interrupted at the proper point, a concentration of viscous products in the residue would take place. This was to be expected from experiments made by Engler on the behaviour of unsaturated compounds, such as amylene and hexylene, when heated under pressure to 300–350° for long periods, and from experiments made in this Institute. Theoretically this might be explained by the thermal decomposition of high molecular compounds to saturated and unsaturated products of low molecular weight, which partly polymerise again, forming compounds of the character of lubricating oils.

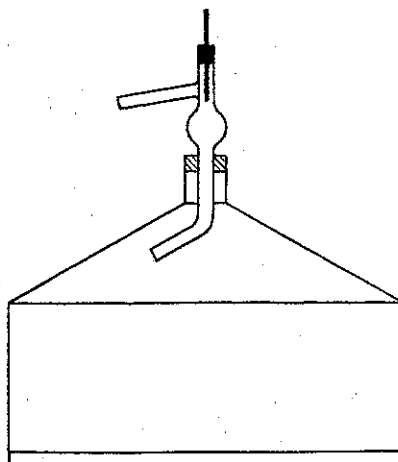
The experiments were performed in a welded sheet-iron still of 1.5 mm. wall thickness, which had done good service before for the distillation of tar in bulk. As to the shape of the still, which has some bearing on the results, it consisted of a cylinder 50 cm. in diameter and about 18 cm. in height, with

a conical top 13 cm. high (Fig. 60). To avoid superheating and to distribute the heat uniformly over the whole of the bottom, the still was not heated by gas burners, but was placed on an electric resistance heater and insulated by porcelain buttons. The cylindrical portion was lagged with a jacket of sheet-iron and asbestos; the conical portion was left bare for the purpose of re-condensing the undecomposed vapours and sending them back into the hot zone. The low-boiling products were taken off through a tube in the top of the cone, which was bent to avoid priming, and were passed through two Liebig condensers and a coil condenser in series. The temperature was taken with a thermometer or thermo-couple in the liquid, 0.5 to 1 cm. from the bottom. Vapour temperatures are not given, as, on account of the very slow distillation, fluctuations in the rate were unavoidable. The distillation was regulated so that a constant and slow drip of distillate was maintained for days without interruption. The specific gravity of the distillates was taken during the experiment as a guide to the progress of decomposition.

These researches have proved that the constituents of primary brown coal tar boiling above  $300^{\circ}$  are broken up to a considerable extent by slow distillation, only about 14 per cent. of the material treated still showing a boiling point above  $300^{\circ}$ . This does not necessarily represent unchanged raw material, but probably contains high-boiling constituents secondarily formed from primary decomposition products.

The bulk (33 per cent.) of the material left after the removal of about 4 per cent. of tar acids and bases, boiled between  $200^{\circ}$  and  $300^{\circ}$ . Seven per cent. of benzine boiling below  $150^{\circ}$ , or 14 per cent. boiling below  $200^{\circ}$ , was obtained. The coke residue amounted to 12 per cent., the difference of about 23 per cent. representing gas and loss. The experiments proved further that a re-formation of high-boiling bodies of lubricating oil character took place simultaneously with the formation of low-boiling products.

The destructive distillation of primary tar from bituminous coal gave similar results.<sup>113</sup> A commercial low-temperature tar containing 45 per cent. phenols, of which 10 litres were submitted to very slow distillation which was continued for 5 days, yielded 5.2 kg. of oil, 3.6 kg. of coke, 2.7 cb.m. of gas and 700 c.c. of water. Fractional redistillation of the oil obtained gave 14 per cent. of benzine boiling below  $200^{\circ}$ , about 40 per cent. of oil from  $200^{\circ}$  to  $250^{\circ}$ , with a phenol content of 45 per cent., about 14 per cent. from



Scale. 1:10.

FIG. 60.

250° to 300°, with a phenol content of 25 per cent., and about 7 per cent. of semi-solid residue suitable for lubricants. The latter substance was formed by polymerisation as in the case of the brown coal tar. Low-boiling phenols do not disappear, but the higher fractions seem to have been diminished.

Considering that almost half of the original tar consisted of phenols, the proportion of low-boiling products obtained could not be very large, for it may be assumed that their parent substance can only be the hydrocarbons of the tar.

*Benzine by Cracking of Primary Tar at Ordinary Pressure.*

As was pointed out in the preceding section, the scission of high-boiling constituents in destructive distillation occurs chiefly in the liquid phase. Since the temperature of the liquid cannot be raised above its boiling point, except when working under pressure, the point of decomposition may not be reached.

If the action on the hydrocarbons is to be intensified at atmospheric pressure, the vapour phase must be superheated, a process known as "cracking." The production of benzine from brown coal tar may be cited as an example.

The pyrogenic decomposition of brown coal tar oils at atmospheric pressure has been the subject of various researches. Several short papers were published in 1878 by C. Liebermann and O. Burg,<sup>114</sup> M. Salzmann and H. Wichelhaus<sup>115</sup> and a few others.<sup>116</sup>

As a result of these investigations it was proved that the pyrogenic decomposition of the less valuable high-boiling fractions of brown coal tar yields products which contain, like ordinary tar, aromatic compounds such as benzene, toluene and anthracene. The most favourable working conditions were investigated.

With a different object in view, the fractions were divided, which makes comparison with our results difficult. The yield of low-boiling products was certainly lower than that realised in the experiments to be described.

In order to facilitate comparisons with the previous work, the raw materials for our experiments<sup>117</sup> were brown coal paraffin and brown coal tar from the Riebeck Montan Works. Further experiments were made with a brown coal producer tar, and with a tar oil fraction boiling between 200° and 300°.

The apparatus used (Fig. 61) consisted of an iron still A of 1 litre capacity, and the superheater tube B (40 cm. long, 5.5 cm. internal diameter) screwed into the cover of A; the cover was clamped to the still, an asbestos joint being interposed. A thermometer well was fixed to the cover with its closed end 1 cm. from bottom of the still. The superheater tube was closed by a screwed plate in which an iron tube was fixed to carry a thermo-couple. The wire gauze netting, on which a catalyst for the superheater was placed in a

layer of 30 cm. thickness, rested on three iron studs fixed immediately above the opening connected to tube D, leading to the cooler E. Another tube C connected the top portion of B with the cooler E, which had approximately the same dimensions as B and was mounted at a distance of 14 cm. from the latter. The tube D was U-shaped and was provided with a drain cock, the liquid collecting in it serving as a seal between E and B. At the top, E was

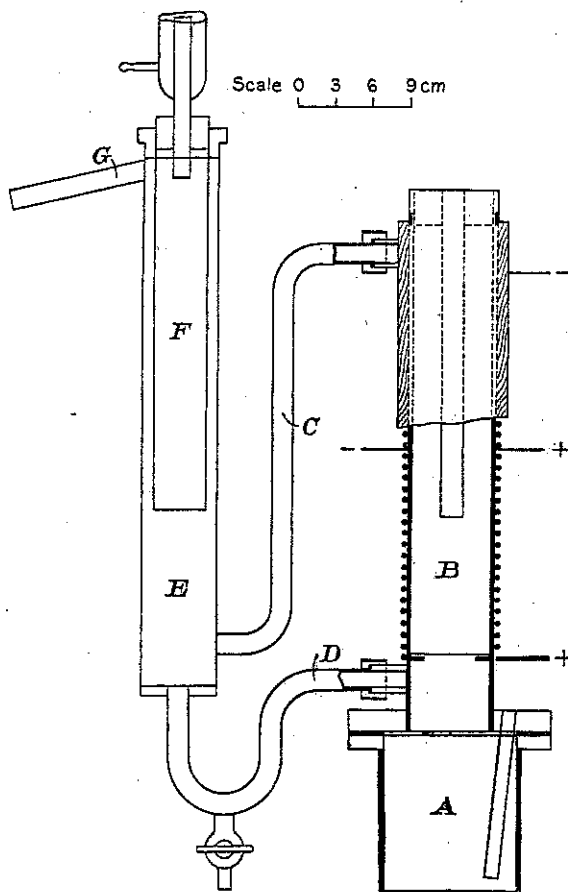


FIG. 61.

closed by a screw plate which was drilled to carry cylinder F, 30 cm. high and 4 cm. internal diameter, with a clearance of 0.8 cm. between its outer wall and the cooler E; it was charged with a liquid of definite boiling point, *e.g.* xylene, so that the vapours rising in E would be cooled to the boiling point of xylene, and only those boiling below this temperature would distil over through take-off tube G. A reflux condenser mounted on F prevented the evaporation of xylene.



The distillation proceeded as follows: The vapours liberated in A passed through the superheated tube B, and then through C into the cooler E. The more volatile constituents escaped through G, whilst the portions of higher boiling range were condensed and returned through D into the superheater B. The latter was electrically heated. Temperatures were first measured by means of a thermo-couple mounted inside the tube. Afterwards two wires of copper and nickel were soldered to the outer wall of G and connected with a millivoltmeter. This did not indicate the highest temperature in the tube, because the turns of the heating coil were pitched farther apart at this point. The hottest portion was about three-quarters of the distance up the tube, where the temperature was from 50° to 60° higher. For purposes of comparison, observation of the wall temperature rendered good service; the maximum temperature was taken at the same time.

After charging the still with tar, and the superheater with the catalyst, the apparatus was assembled; container F was filled with xylene and fitted with a cork stopper which carried a Liebig condenser. Another Liebig condenser was joined to the off-take G, and was connected by an adapter to a flask serving as first receiver. The second receiver was an Erlenmeyer flask, the inlet tube of which reached close to the bottom. These two receivers were cooled by means of a freezing mixture. There followed a third vessel, cooled in some experiments by means of liquid air, and finally a gas meter. The iron still, which was surrounded by a protective shield, was heated by means of gas burners, and the superheater was brought up to 400° at the same time. After the liquid had started boiling, the temperature of B was gradually raised until the appearance of white, more or less dense fumes and the escape of gases indicated decomposition. As soon as the temperature dropped, the formation of fumes ceased; if it rose too high, they turned brown. These signs facilitated the maintenance of the correct temperature range. This was not always easy, because the gradual increase in temperature required, for instance, in the case of brown coal tar, caused fluctuations in the vapour velocity through B, and hence temperature variations. Yet the apparatus worked satisfactorily enough for comparative experiments. It was noticed that the gases carried a good deal of high-boiling products through the cooling tube. The substitution of water for xylene made as little difference as the charging of the cooling tube with broken brick, which ought to have facilitated fractionation owing to its great surface.\* Heating was continued until the bottom of the still was red hot and the still contained only coke. After completion of the experiment, the liquid still contained in D was drawn off by means of the tap. In the tables

\* Although broken brick, on account of porosity, was not very suitable for this purpose, a preliminary experiment showed that the temperature inside the cooling tube at a level with the take-off was about 68-70°. Yet, the condensate consisted of about equal fractions boiling below and above 200°. The generation of gas prevented a proper fractionation.

this portion of the liquid is termed "liquid" residue. An experiment took from two to three hours. The distillates in the two receivers were weighed and combined. Very little liquid was usually found in the second receiver, at the utmost 5 per cent. of the total distillate. The coke was taken from the still at the end of each experiment, and weighed.

TABLE XLII

Raw material.	Superheater tube B charged with broken brick.		Superheater tube empty.		
	Paraffin wax.	Carbonising tar from Central German brown coal distilled to 200°.		Carbonising tar.	
		Expt. I.	Expt. II.	Expt. I.	Expt. II.
Quantity used . . . . .	200 g.	360 g.	205 g.	329 g.	214 g.
Total distillate . . . . .	51.8%	53.2%	50.2%	47%	55%
Liquid residue in apparatus	6%	4.2%	6.3%	3%	5.6%
Coke residue in still . . . .	0.8%	8.1%	8.6%	9.4%	6.5%
Gases condensed with liquid air . . . . .	36.4%	20.6%	29.9%	25.8%	—
Measured in gas meter . . .	8.5 l.	15 l.	13 l.	14 l.	45 l.

Results of Fractionation of Total Distillate obtained.

40-100°	20.5%	} 17.1%	10.0%	8.7%	6.2%
100-150°	13.9%		6.5%	7.7%	7.3%
150-200°	11.4%		8.4%	10.2%	10.4%
200-300°	} 5.6%		18.9%	} 20.3%	32.8%
above 300°			6.6%		

In testing the catalytic effect of various catalysts, we impregnated broken brick of nut size with a concentrated solution of the substances and expelled the water either in a drying oven, or, preferably, in the superheater before assembling our apparatus. The mode of procedure was the same as before. The raw material in these comparative experiments was a lignite tar, from which the fractions boiling below 200° had been distilled off. The catalysts enumerated in Table XLIII had no appreciable influence upon the temperature of decomposition. It would therefore appear that the decomposition must be regarded as a purely thermal process. The effective temperature measured at the wall in these experiments was as in the previous ones, between 530° and 560°.

Table XLIII shows that the yield of products boiling below 150° amounted to 14-16 per cent., and that of the products below 200° to 24-28 per cent. The

TABLE XLIII

*Summary of Experiments on Decomposition of Brown Coal Tar in the presence of Catalysts*

Catalyst	Al	Fe	Coke	Bauxite	NaOH	H <sub>3</sub> PO <sub>4</sub>	MnCl <sub>2</sub>	CrCl <sub>3</sub>	BaCl <sub>2</sub> *	ZnCl <sub>2</sub>
	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.
Total dis- tillate .	43.2	48	51	53	54	46	49.5	42.6	43	24
Residue .	3.4	8.8	9.5	3.1	9.4	5.4	8.5	7.4	—	45
Coke . .	13	9.5	7.4	5.1	6.7	13.7	8	7.4	—	{ 8.3 <sup>†</sup> 15 <sup>‡</sup>
Condensed in liquid air . .	23.2	—	—	14.3	20.3	—	—	26.9	—	—
Measured in gas meter	22 l.	48 l.	51 l.	66 l.	13 l.	49 l.	—	18 l.	46 l.	32 l.

Results of Fractionation of Total Distillate.

below 100°	7.9	8.2	7.6	7.0	7.1	8.3	7.1	7.7	6	3.2
100-150°	7.3	7.2	6.6	8.8	7.0	7.3	6.7	5.6	5	2.4
150-200°	8.2	10.1	9.0	11.6	10.7	8.3	11.8	9.3	6	5.9
200-300°	12.9	16.5	17.0	19.1	22.1	14.1	16.8	15.0	} 23	4.9
above 300°	4.4	8.8	10.0	5.2	10.2	6.3	8.2	5.3		1.9

fluctuations within these narrow limits are hardly due to specific effects of the catalysts, but chiefly to difficulties in controlling experimental conditions. § Chromic chloride and zinc chloride catalysts behaved somewhat differently. With the former, some coking took place in the superheater. With zinc chloride, coking was so pronounced that part of the superheater was completely blocked. For that reason the total distillate amounted only to about 25 per cent., while 50 per cent. of oil was withdrawn from the U-tube. The coke in the superheater amounted to about 15 per cent. It is known that thick viscous oils are formed on boiling brown coal tar oil with zinc chloride. Similar reactions probably occur in the superheater tube and lead to the copious deposition of coke.

Briefly recapitulating the results of these experiments, it is shown, in accordance with other researches, that decomposition by superheating at atmospheric pressure favours the liberation of gases to an extraordinary degree. The catalysts used had no appreciable influence either on the temperature of decomposition or on the yields. The experiments with brown coal tar gave on average 15 per cent. of benzine boiling from 35° to

\* This experiment was not completed, being very similar to that with MnCl<sub>2</sub>.

† In the still.

‡ In the catalyst tube.

§ It is not known whether the iodine numbers of corresponding fractions tally; for other purposes these fractions were combined to be worked up.

150°, as against 25 per cent. with application of pressure. 3 to 4 per cent. of the benzine was carried away with the gases. The products obtained resembled in smell and in appearance those resulting from heating under pressure, but the specific gravity was somewhat higher, and they differed from the latter products in their extremely high percentage of unsaturated compounds. The products could be readily refined, as regards smell and colour, by treatment with caustic soda, and more effectively with zinc chloride.

In the selection of the raw material for these decomposition processes preference will naturally be given, not to the primary tars of brown coal rich in bitumen, which can be more economically worked up for paraffin, but to the primary tars obtained from coal poor in bitumen, which by improvements in plant are produced in ever-increasing quantity and of superior quality.

Corresponding experiments on primary tar from bituminous coal have not yet been published. This tar should, on cracking, behave similarly to the primary tar from brown coal, but would probably differ by a still lower proportion of cracked benzines, owing to its lower hydrocarbon content. Phenols, when their vapours are superheated, do not yield benzine any more than by decomposition of the liquid phase, as has been shown in the last section.

Superheating experiments with primary tar from bituminous coal at ordinary pressure have been made under somewhat different conditions. It was then found <sup>118</sup> that the carbolic acid, originally present only in small quantity, was increased by the decomposition of higher-boiling phenols. The appearance of acetone in some commercial primary tars from coal may also be due to superheating. For no acetone was found in the primary tar carefully prepared from the same coal in the laboratory rotating drum.<sup>47</sup> That the primary tar from coal is highly sensitive to distillation, even at ordinary temperature, was mentioned on p. 93.

There appears to be no possibility of hydrogenating tar or tar oils at temperatures between 300° and 500° without the application of high pressure, even when catalysts are used. Catalysts are not likely to induce sufficient hydrogenation to counteract the liability to scission of hydrogen at these temperatures.

I therefore regard the process of Melamid,<sup>119</sup> who sprays the material to be hydrogenated by means of hydrogen into hot reaction chambers containing catalysts, merely as a cracking process, though the addition of hydrogen may possibly be an advantageous modification. It is not impossible that an atmosphere of hydrogen alone at ordinary pressure would suppress the liberation of hydrogen from the oil, and that limiting the reaction time would lead to molecular fragments richer in hydrogen.

The process of Melamid is mentioned here as being, in my opinion, a modified cracking process at ordinary pressure.

*Benzine by Cracking under Pressure.*

The observation that high-boiling, solid hydrocarbons of the paraffin series, by being heated in closed vessels, are split into liquid products of lower boiling points with a small evolution of gas, was made long ago by Thorpe and Young.<sup>120</sup> These investigators distilled paraffin wax from the hot portion into the cold portion of a two-limb closed tube, and observed that the paraffin wax after repeated distillation had assumed the consistency of butter and could be liquefied by the heat of the hand, and that after twelve distillations the bulk of the products remained liquid at ordinary temperature.

Similar reactions have been applied in the petroleum industry, particularly in America, for the purpose of converting heavy high-boiling oils into lighter lower-boiling oils. The original object was to increase the yield in lamp oil, but of late years petrol production has been the object. The consumption of motor spirit has increased to an extraordinary extent, whilst the production of oils of the paraffin type has decreased in the Eastern American States, though the production of asphaltic oils has much increased in California and Mexico. The former type of petroleum yields ample proportions of petrol. The latter contains much smaller quantities of lower-boiling constituents, or none at all.<sup>121</sup> The destructive distillation or cracking, introduced for the purpose of splitting hydrocarbons of high molecular weight into compounds of lower molecular weight, is based upon scission of the molecules by superheating, and it necessitates subjecting the oils either to prolonged heating or to heating at considerably higher temperatures. Conducted at atmospheric pressure this mode of procedure yielded favourable results, as long as the object aimed at was an increased production of kerosene, but it does not appear to have been found satisfactory for the production of petrol. Distillation under pressure was therefore resorted to; although this treatment does not yield a benzine of full value, the low-boiling product obtained is an acceptable substitute, and this mode of cracking has by now been practised for a long time in the American Oil Industry. Some two million gallons per day of benzine are produced in this way by the Burton<sup>122</sup> process. This application of distillation under pressure is not new. Young applied it in his factory fifty years ago, and Krey in Germany worked out patents in 1887 for the production of lamp oils from the heavy paraffin oils of brown coal tar by distilling the high-boiling constituents under a pressure of 6 atm. For economic reasons the process did not come into continued operation at that time, nor did the process of Graefe and von Walther, who used much higher pressures for the decomposition of brown coal tars.

The nature of the reactions involved in this destructive distillation remains on the whole obscure. It is certain that the chains of the larger molecules are split into fragments of lower molecular weight with partial formation of

unsaturated compounds, and that there is, on the other hand, polymerisation of very small fragments to compounds of greater size. In the ordinary decomposition by distillation, the molecules are split near the ends of chains, and gases and oils of relatively high molecular weight are formed. When pressure is applied the splitting takes place nearer the middle of the chain.<sup>123</sup>

An autoclave of 1.2 litres capacity was filled to about one-third or half its volume.<sup>124</sup> A pressure gauge, a long thermometer sheath dipping into the liquid, and an outlet tube were attached to the cover of the autoclave.

According to Snelling,<sup>125</sup> heating of paraffin wax under pressure gives the best results when the vessel is more than one-tenth, but less than half full. The autoclave was rapidly heated by three burners, and the temperature in the vessel was read as soon as pressure was set up, heating being continued until the desired pressure had been attained. After complete cooling and discharge of the gas, the contents of the autoclave were distilled, and the products passing over below 150° were well cooled by means of a freezing mixture. During this distillation, temperature readings were taken immediately below the cover. The residue at 150° was then several times submitted to the same heating process in the autoclave. For the sake of simplicity oils boiling below 100° may be called light benzines; the fractions 100° to 150°, heavy benzines; and the fractions 150° to 300°, middle oils. It need hardly be pointed out that the products so designated are not identical with the benzine fractions which are obtained from petroleum, and which contain large quantities of unsaturated compounds.

TABLE XLIV

*Experiment with Brown Coal Tar*

Used: 500 grams Tar

Repeated heating.	Approx. duration of heating up to beginning of pressure. Min.	Temp. at beginning of pressure. °C.	Heating period from beginning of pressure to maximum pressure. Min.	Maximum pressure. Atm.	Pressure after heating. Atm.	Distilled below 150°. g.
I.	15	300	20	29	1-2	33.0
II.	15	350	25	32	4	41.6
III.	15	345	30	30	4	32.7
IV.	10	320	45	30	3	30.3
V.	20	320	43	33	2	26.0
VI.	20	293	50	32	2	23.0
						186.6

After heating six times, the autoclave was opened, the liquid was syphoned off, and the residue, which at the bottom formed an adhering coke, but was loose and still moist in the upper part, was weighed.

Raw products obtained :—

(i) distilled from the autoclave up to 150°	187	grams
(ii) syphoned off	176	„
(iii) coke residue	60	„
Total	423	„

The total yield of 423 grams of weighable products represents about 85 per cent. Liquid (ii), on standing for some time, deposited 30 grams of tarry matter. The fractional distillation of 177 grams of liquid (i) yielded, after separation of water :—

(1) 40–100°	58	grams.
(2) 100–150°	68	„
(3) residue boiling above 300°	50	„

Liquid (iii) was added to the oil syphoned from the autoclave, and distilled; the fractions were :—

150–200°	54.2	grams.
200–300°	90.0	„
above 300°	50.0	„

The total result is therefore the following :—

500 Grams of brown coal tar yielded 11.6 per cent. of light benzine, 13.6 per cent. of heavy benzine, 29 per cent. of middle oil, 10 per cent. of constituents boiling above 300°, 2 per cent. water, 6 per cent. tarry matter, and 12 per cent. of coke; a total of 84.2 per cent.

The properties of these products were as follows :—

(1) *Light Benzine*.—The distillate which was originally almost colourless turned gradually pink and darkened more and more. After six days some red-coloured matter had deposited on the walls and on the bottom of the receiver. The liquid itself had now only a faint yellow colour and a faint unpleasant smell.

(2) *Heavy Benzine*.—This fraction also gradually turned to a pink colour. The colour then changed into a light brown, and there was some deposit on the walls of the receiver. The liquid finally was darker than the oil (i).

(3) *Middle Oil*.—The middle oil had a reddish-brown colour.

The following table records the results obtained with, and without, pressure :—

	Ordinary distillation.	After repeated heating under pressure.
Below 100° . . . . .	0.5%	11.6%
100-150° . . . . .	1.1%	13.6%
150-200° . . . . .	8.7%	11.0%
200-300° . . . . .	35.7%	18.0%

	Light benzine.	Heavy benzine.	Middle oil.
Spec. grav. at 22° . . . . .	0.684	0.765	0.844
Calorific value (Berthelot-Mahler Bomb) . . . . .	10399	10853	10636 cal.
Flash point (Pensky-Martens) . . . . .	below 30°	below 30°	41°
Iodine number (Hübl) . . . . .	69	64	39

The iodine number of heavy benzine from ordinary brown coal tar (obtained without heating under pressure) is, according to Graefe,<sup>126</sup> 61 before and 59 after treatment with  $\text{H}_2\text{SO}_4$ .

Our iodine values were determined on products which had been kept standing for a year for another purpose, and were then poured off from the resinous deposit, and redistilled. The iodine numbers tabulated above are, therefore, not directly comparable with those of freshly prepared products.

Under the conditions of repeated heating under pressure, brown coal tar yields considerably higher quantities of low-boiling products than by destructive distillation, or by cracking at ordinary pressure. The products are at the same time superior to those from the latter two processes. The highest yield of low-boiling products is obtained from those primary or ordinary brown coal tars which are poorest in phenolic constituents, and, therefore, richest in viscous oils and paraffin wax.

The commercial production of benzine from brown coal tar is, of course, not conducted in the above-described primitive way of alternate heating in an autoclave and redistillation of the low-boiling products. The process must be continuous, the liquid being discharged from the autoclave while still hot, and the apparatus should be so arranged that the low-boiling constituents are boiled off and condensed, whilst the higher-boiling constituents are returned to the autoclave, possibly mixed with a suitable quantity of fresh tar. The same treatment may be applied to fractions of brown coal tar, which should be particularly suited for benzine recovery.

A technical process of this class is Blümner's,<sup>127</sup> in which an exact maintenance of the optimum temperature of 450° to 500° is ensured by forcing tar



through an autoclave which is charged with contact rings and molten metal. The tar bubbles are evenly distributed by the contact rings through the molten metal, without coming into contact with the steel shell, where they would be superheated. Fig. 62 shows diagrammatically the arrangement of the apparatus.<sup>128</sup> Whether the Blümner process will prove superior to the pressure cracking processes, which have been developed in the United States, and have stood the practical test, remains to be seen, also whether this method will yield only a small proportion of unsaturated hydrocarbons, as Burton claims for his process. The Burton process could no doubt be used for the production of benzine from primary tars and tar oils. The characteristic points of this process may therefore be outlined.

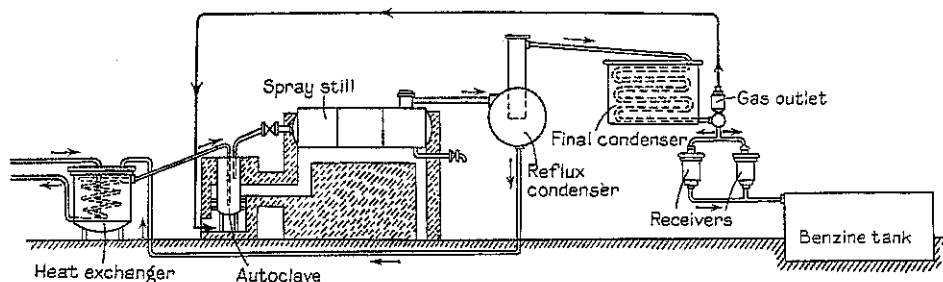


FIG. 62.

### *Benzine by the Burton Process* <sup>129</sup>

The preparation of benzine by cracking under pressure gives less unsaturated compounds than when pressure is not applied.

In the method described above, pressure is set up by the vapours and gases liberated during the process. The cracking process is therefore started without pressure or, at any rate, without high gas pressure, this being developed during the experiment by the evolution of gas.

The Burton process differs from the above described in that the plant is started up with initial pressure. The permanent gases, which are liberated in every cracking process, are collected by Burton and forced by a compressor into the still at the beginning of a run, as soon as the removal of water from the oil is complete. The pressure applied is stated to be only 5 atm. Heating is continued under this pressure up to the cracking temperature, and as a result, the gasoline is claimed to be almost free from unsaturated compounds. The statements as to pressure and freedom from unsaturated compounds cannot be vouched for. Burton's process is distinguished from other cracking processes in use; he ingeniously presses the advantage of working under pressure to its logical conclusion, starting with compressed gas from the very beginning in order to obviate any tendency to decomposition. It is conceivable that the bulk of unsaturated hydrocarbons is formed in other cracking processes during

the first stage, when the gas pressure is not high enough. If this view be correct, Burton's claim that his gasoline is better than others is perfectly intelligible. It would certainly be desirable to examine samples taken at different stages of the ordinary cracking processes for their degree of unsaturation of the benzines produced in relation to the pressure curve.

*Benzine by Cracking and Simultaneous Hydrogenation under High Pressure*

All benzines produced by cracking labour under the disadvantage of a high content of unsaturated compounds, which gives them an unpleasant smell and the undesirable property of darkening and gumming. This drawback seems to be partly or wholly avoided in the "Bergin" process, which Bergius<sup>130</sup> worked out and brought to a stage of high technical perfection in a large experimental plant at Rheinau, near Mannheim. Whether the yields of benzine from the same raw materials are greater than, for instance, in the Blümner process, can only be decided by exact comparative experiments. The part played by the hydrogen, which in the Bergin process is applied at a pressure of 100 atm., may be two-fold. The primary reaction in the Bergin process is probably the same as in any other cracking process. It is, however, conceivable that not only hydrogenation of nascent unsaturated compounds occurs, with suppression of the formation of coke, but also that the increase in total pressure caused by the hydrogen is of importance. It was stated, on p. 147, that in cracking under pressure the hydrocarbon chains are split about their middle with formation of liquid hydrocarbons, whilst at ordinary pressure scission takes place nearer the end of the chain, with copious evolution of gas. It is, therefore, quite plausible that the Bergin process with its high pressure more nearly approaches the object for which pressure is applied, and that it will therefore yield more liquid hydrocarbons and correspondingly less gas. Experiments with the Bergin process have so far mainly been made with petroleum products, but there is also some information on the Berginisation of tars. The impression given by statements that a practically complete\* splitting-up of heavy oils into benzines is possible has not yet been confirmed.<sup>131</sup> This may, according to all experience, hold for certain selected and specially suitable fractions, but not for heavy oils generally. The laboratory apparatus which Bergius uses in his hydrogenation process, termed Berginisation, has a capacity of about 5 litres and is heated with gas. Temperatures are measured by means of a thermo-couple placed in the axial tube closed at one end. Fig. 63 shows diagrammatically the arrangement of the apparatus.

Bergius gives the following details of the method of working: "In making experiments in the 5-litre bomb, the vessel is gripped in a vice and charged with the weighed quantity of raw material. The cover is then put on, and the

\* The loss by formation of permanent gases is stated not to exceed a few per cent.

vessel is mounted on plummer blocks, and is connected with the hydrogen feed-pipe and filled with the desired amount of hydrogen as measured by a gauge. After closing the valve, the hydrogen pipe is disconnected; the thermo-couple is inserted into the inner tube, and the apparatus is rotated.

A temperature record is always kept for the control of the apparatus. The gas burners and pressure gauge are watched from outside. After a given time the heating gas is turned off and the apparatus is allowed to cool; the bomb is then again put into the vice and the gas pressure is released. The gases are collected in a gasholder, and are examined for condensable and non-condensable hydrocarbons. The cover is then removed, and the contents of the bomb poured out and worked-up. The pouring losses may be estimated from experience. Part of the losses is due to matter adhering to the walls of the bomb; another portion consists of condensable gases which are present in the relatively large volume of unconsumed hydrogen. These losses can be determined by cooling or washing.

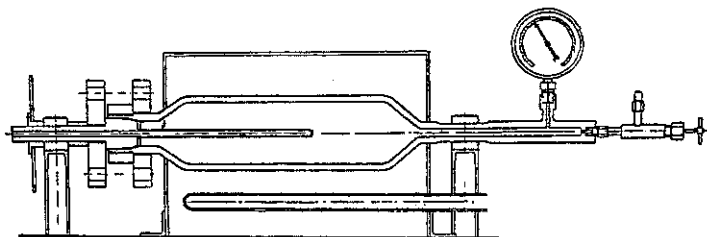


FIG. 63.

" This intermittent mode of working served us and is still being used for, the technical study of the hydrogenation of various raw materials. For industrial uses the method is manifestly not suitable; for these a continuous method had to be worked out. A continuous apparatus was used by us at Hanover as early as 1914, and has since been further developed. Fig. 64 explains the arrangement now in use. Hydrogen is circulated by means of a pump through the high-pressure apparatus, and serves both as a reacting medium and as a carrier for the resultant products. The hydrogen and the raw material, which is forced into the apparatus by a pressure pump, are first heated in a separate preheater to the working temperature in order that the reaction chamber itself may be properly utilised. The reaction vessel is a steel cylinder of about 40 litres capacity, fitted with stirring gear. The raw material and hydrogen enter at one end, and hydrogen charged with oil vapours leaves at the other end. A reflux condenser returns the entrained heavy products into the apparatus, whilst the lighter products are condensed, collected in a pressure vessel and separated from hydrogen. The cooled hydrogen returns to the pump, and is again fed into the apparatus after having passed through the preheater. The products are discharged from the

receiver in which they are kept under working pressure, and are separated from the dissolved gases which are liberated on expansion. A lead bath supplies the heat required for heating-up and for maintaining the temperature."

A commercial plant is now in operation at Rheinau, of 4 cb. m. reaction space and a rated capacity of 20,000 tons of raw material per annum. The numerous visitors to this installation speak most highly of the supreme excellence of the mechanical arrangements. The reaction chamber is double-walled, and is heated by forcing hot compressed nitrogen through the jacket space and back to the heater disposed in a lead bath. Several advantages are claimed for this mode of heating. The nitrogen, being under pressure, compensates hydrogen pressure on the inner wall of the reaction chamber. This pressure-balance is particularly desirable, as compressed hydrogen at a

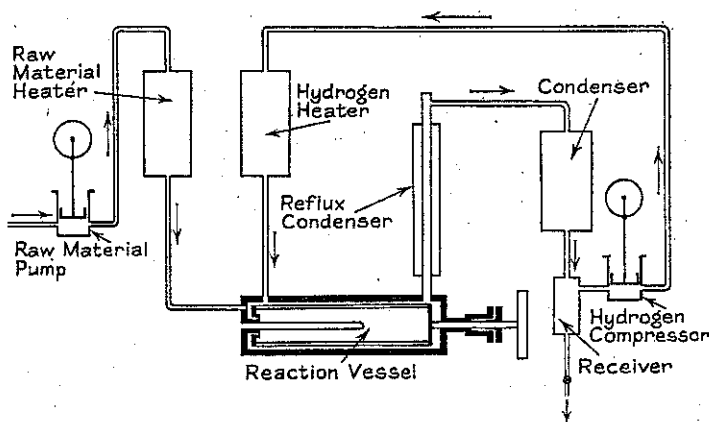


FIG. 64.

temperature of  $400^{\circ}$  dissolves carbon in the form of methane from the iron and steel, thereby diminishing the tensile strength of the metals. The outer wall of the reaction chamber, which has to bear the pressure difference against the atmospheric, is not endangered by the chemical action, being in contact with compressed nitrogen.

A maximum margin of safety in working is claimed for this arrangement against the risk of fracture of the walls. Provision is further made that the nitrogen in the jacket is at all times at somewhat higher pressure than the hydrogen in the chamber, so that in case of any damage to the inner wall, which is slightly thinner than the outer wall, there would be no escape of hydrogen, but the nitrogen would rush into the chamber. The installation is fitted with the requisite heat exchangers.

The arrangements for the production of hydrogen do not come within the scope of this work, but the results obtained with producer tar from brown coal are of great interest.

TABLE XLV  
*Brown Coal Producer Tar*

Density = 1.045. Solidification point = 28°.

Ordinary distillation.	110-300°	>300°. Solidif. pt. 38°. Density = 1.042.	
After Berginisation.	Berginol. Visc. = 1.35° E. Density = 0.922		
After distillation of Berginol.	75-210°	210-300°	>300° Solidif. pt. 15°. Density = 1.04
<div><div></div><div>20</div><div>40</div><div>60</div><div>80</div><div>100 kg</div></div>			

According to Table XLV, which is taken from the paper by Bergius, 100 kg. of producer tar from brown coal yielded on Berginisation the following results : 25 kg. of oil boiling from 75° to 210°, which may be called benzine, and about 40 kg. of oil, boiling from 210° to 300°. The difference of 35 kg. includes oils boiling above 300°, of solidification point 15° and density 1.04, and loss. The loss cannot well be estimated, as the total weight of the resultant liquid products cannot be clearly seen from the table, but there certainly was some loss. It is not possible to see from the table whether the Bergius process would be capable of converting, by repeated treatment, the high-boiling portion completely into benzine, *i.e.*, whether 100 kg. of brown coal producer tar would yield 100 kg. of benzine. According to the general experience of cracking brown coal tar under pressure, which process gives the best yields, one may expect a maximum of 35 per cent. benzine boiling below 200°. Bergius's value of 24 per cent. for benzine boiling below 210°, or say 20 per cent. below 200°, lies far below the figure of 35 per cent. The reason may be that the table gives results of a single treatment. With repeated treatments of the residue the benzine yield would be higher. This assumed analogy between the processes of cracking under pressure and of Berginisation is unfortunately not explained by the graph (Fig. 65), which gives the pressure curves for cracking and Berginisation. The diagram shows that the pressure rise in the Berginisation ceases with the end of the heating-up period, and that at constant temperature a slow diminution of pressure takes place, due to the absorption of hydrogen by the unsaturated compounds formed by cracking, and doubtless also to the formation of methane. The significance of the methane formation will be discussed in connection with the hydrogenation of coal by means of hydrogen. The corresponding pressure curve of the cracking process shows a continuous rise. This rise will presumably continue until a pressure is reached which prevents the further liberation of gases at a given temperature. If the cracking experiments had been made with a more complete filling of the reaction chamber (attention has been drawn by Snelling to the importance of free space in the

autoclave, see p. 147), the pressure rise would have been much more rapid. If enough tar had been put into the autoclave to leave only a quarter of the gas space allowed by Bergius, the pressure curve would have approached the Berginisation curve more closely. The difference would be that the curve would commence at zero, as the initial hydrogen pressure of 100 atm. would be missing, and the pressure would eventually remain constant and not show a drop.

A comparative study of the pressure cracking process and Berginisation is exceedingly interesting. For a strict comparison, the cracking should begin with a nitrogen pressure of 100 atm., as Bergius commences with hydrogen at that pressure; the pressure curves, as well as the products obtained, could then be directly compared. This has not yet been done, although the reaction

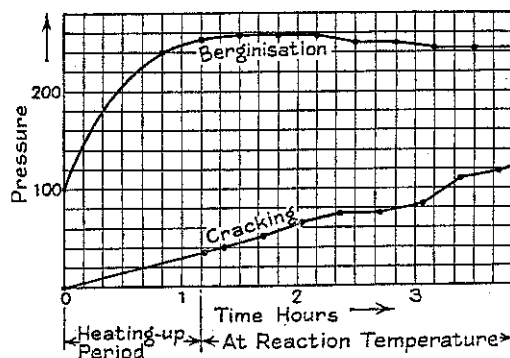


FIG. 65.—Typical pressure diagram comparing Berginisation and cracking experiments at approximately equal temperature.

would not be seriously disturbed by the formation of ammonia from nitrogen at these temperatures. If such data were available, the hydrogen consumption of Berginisation and its nature generally would become much more apparent.

A paper by Waterman and Perquin,<sup>132</sup> on comparative experiments with cracking under pressure and Berginisation, is an interesting contribution to this problem. The paper deals with the behaviour of paraffin wax,\* and is here of interest for the study of the behaviour of brown coal tar, because paraffin wax is an essential component of this tar and of all its constituents that give the best benzine yields on cracking. The paraffin applied had the following properties:  $D^{15} = 0.913$ , solidifying point  $50.6^{\circ}$ , bromine value 0.5.

300 Grams of paraffin wax and 300 grams of pebbles were shaken in a steel autoclave which was heated to  $435^{\circ}$  and maintained at this temperature. The pressure rose continuously in the way indicated by Bergius. The corresponding

\* Berginisation would show up better in the case of asphalt, which cannot be cracked to oil and gas as readily as paraffin wax.

experiment, according to Bergius, was made with an initial hydrogen pressure of 40 atm., as Fig. 66 and Table XLVI show. The curve becomes flatter, once temperature has become constant, but there is no indication of a decrease of pressure after 4 hours. The initial pressure of 40 atm. applied by Waterman may have been too low, and the reaction therefore too slow. Bergius, in the experiment illustrated by the graph, used an initial hydrogen pressure of 100 atm. Possibly the absence of the accelerating effect of the iron oxide, about 5 per cent. of which Bergius always adds, made itself felt, although, according to Bergius, this oxide is not to act as a catalyst but simply as a desulphuring agent—a statement which could easily be verified by experiment.

Possibly Waterman's temperature was too high. He may have adopted a high temperature in order to accelerate the reaction, other accelerating factors

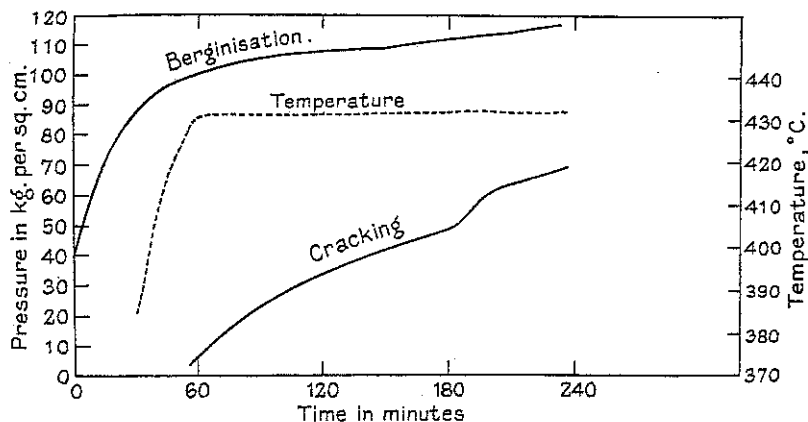


FIG. 66.

being insufficient. An argument against this latter assumption is the fact that Waterman was perfectly aware of the importance of maintaining exact temperature limits.

He states (*Chimie et Industrie*, Numéro special, May 1913), at the conclusion of his paper, that the influence of temperature upon the reactions is very important. In the Berginisation of a fraction ( $D = 0.993$ ) of a heavy asphaltic oil from Borneo, he had observed, when using a stationary autoclave, that a temperature of  $388^{\circ}$  was too low, and  $420^{\circ}$  too high. Fairly favourable results had been obtained between  $403^{\circ}$  and  $410^{\circ}$ . At too high a temperature (in his case  $420^{\circ}$ ) the cracking process predominated; at too low a temperature the intensity of the Berginisation was too feeble, because at that temperature cracking (a necessary preliminary then) was still inappreciable.

It is further known that the optimum temperature varies with the raw material. This is intelligible, for the thermal decomposition (cracking)

TABLE XLVI

*Comparison of Berginisation and Cracking at + 435°*

No. of the experiment.	Time required to reach the temperature in minutes.	Duration of the proper experiment in minutes.	Initial pressure in atmospheres.	Maximum pressure during the experiment.	Final pressure after complete cooling.	Obtained oils in grams.	Bromine content (addition).	Distillation of the oil obtained according to Engler.					Gases.		
								Weight % of the distilled oil.				Sp. G. residue 15°/15°.	Quan- tity in Litres.	Sp. Gr. com- pared with air.	Hydro- gen %.
								to 220°.	to 300°.	residue > 300°.	Loss.†				
Berginisation 35 37 36 33 46 48	60	60	40	110.5	37.5	260 *	16.4	24.9	41.0	56.3	2.7	0.846	—	0.24	85.8
	60	60	40	108.5	37.5	272 *	16.1	22.8	37.9	59.0	3.1	0.854	—	0.20	89.5
	60	120	40	107	31	272	19.0	36.6	56.6	38.7	4.7	0.838	—	0.37	74.6
	60	180	40	117	30	256	20.8	51.7	72.1	22.4	5.5	0.852	—	0.56	56.9
	75	240	40	118	28	250	21.0	58.9	79.6	14.8	5.6	0.836	63	0.63	47.5
	75	240	40	120	28	249	20.7	59.7	79.2	13.8	7.0	0.838	62.5	0.63	46.5
Cracking 40 45 34 49	80	60	0	30	± 2	271 *	21.6	23.0	39.0	60.1	0.9	0.854	—	0.99	—
	70	120	0	51.5	< 4	270	27.6	41.9	63.7	32.0	4.3	0.855	—	0.80	—
	60	180	0	71	5	246	26.1	56.5	76.5	17.5	6.0	0.900	—	1.10	2.3
	75	240	0	72	7.5	238	23.9	56.8	76.9	16.2	6.9	0.902	29	0.94	3.7

\* The product obtained was still solid and had to be melted out, which gave rise to extra losses of weight.

† Belongs to the lowest fraction.



of different kinds of molecules of the various raw materials sets in at different temperatures,\* and only then can Berginisation take place.

The result of Waterman's experiments was that all paraffin wax was invariably converted into oil and gas, whether he worked under hydrogen pressure or not. Further, the yields of benzine were the same in both cases. The density was, however, always lower in the Bergius experiments than in the corresponding cracking tests, as Table XLVI shows.

The final pressure in the Bergius experiments, which was always lower than the initial pressure, as well as the composition of the resulting gases, demonstrate that a considerable proportion of the hydrogen had been consumed. The bromine value of the products, *i.e.*, their degree of unsaturation, was smaller with the Bergius process than with the cracking process.

Although it would have been better in the experiments both of Waterman and of Bergius if cracking had been tried with an initial nitrogen pressure of 40 atm. (argon would have been still better), the comparison demonstrates that the benzine yields did not differ in the two cases. The products differed only as to quality, a fact which confirms an assumption expressed on a previous occasion.<sup>133</sup>

There was no noteworthy difference as regards the deposition of "carbon," which was very small in both cases. In this respect, paraffin wax seems less suitable for comparison than asphalt, for instance. All the same, the experiments of Waterman are very valuable for the study of the Bergius process.

In mixtures of compounds such as tars and tar oils, hydrogenation is, of course, not limited to the saturation of unsaturated fragments of molecules formed by cracking. A reduction of oxygenated compounds to hydrocarbons is likewise conceivable, and a hydrogenation of the same, *e.g.*, of the phenols, to hydro-aromatic alcohols is still more probable. This problem will be discussed in the following sections.

#### 6. *The Hydrogenation of Primary Tars, Tar Oils and Phenols*

##### *With Catalysts.*

A more complete hydrogenation of the constituents of primary tars and tar oils would no doubt be possible if one could work at temperatures considerably below the temperature of 400°, at which Bergius operates. Without the use of catalysts the reaction velocity is, however, too small at temperatures between 200° and 300°. In practice, one would be compelled to work, as in the manufacture of tetralin, at these lower temperatures with the aid of hydrogen under strong pressure, and finely divided nickel as catalyst. As the nickel catalyst is poisoned very quickly by sulphur, the tar oils must be submitted to an intensive preliminary purification for the elimination of sulphur com-

\* There is surely an analogy with ignition points, which are preceded by a loosening of the molecules.

pounds. In the preparation of naphthalene for hydrogenation into tetrahydronaphthalene (tetralin), this purification is effected by means of metallic sodium with perfect success, but only after thorough refining of the naphthalene by physical processes.

Preliminary purification of the tar oils by means of crystallisation need hardly be considered. A purification with sodium could only be applied to the hydrocarbon fraction of the tar oils, and would necessitate the previous separation of the phenols. In the presence of phenols in tar oils, which may contain one-half of them, metallic sodium would simply dissolve with generation of hydrogen and formation of phenolates, and the consumption of sodium would assume fantastic dimensions. Considering all these factors, it will be seen that the hydrogenation of the technical tar oils by means of catalysts is practically out of the question. Recognition of this fact may explain why the Tetralin Works at Rotleben have acquired a licence under the Bergius patents for the industrial hydrogenation of tar products rich in sulphur, which, owing to this sulphur and to their general properties, are not amenable to purification by catalysts.

#### *Without Catalysts.*

To carry out the hydrogenation without the aid of catalysts requires, as has already been explained, temperatures near  $400^{\circ}$ , say between  $350^{\circ}$  and  $450^{\circ}$ , to ensure a measurable reaction velocity. Since, however, hydrocarbons rich in hydrogen, hydro-aromatic or aliphatic, are very liable, even at these temperatures, to split off hydrogen and to be converted into compounds poorer in hydrogen, hydrogenation can only be successful if conducted under hydrogen pressures which exceed the dissociation pressure of hydrogen in the products to be formed at any given temperature of reaction. Thus, one is compelled towards hydrogenation at high pressure, as first applied by Ipatiew to numerous compounds, and later by Bergius to mixtures such as commercial oils and coal. The latter process, as has been pointed out, is really a continuation of hydrogenation with preliminary cracking.

Scientific information concerning the real nature of hydrogenation by the Bergius process not being available so far, we can only communicate the results obtained in the hydrogenation of primary tar oils and primary tar phenols by the aid of sodium formate, and with carbon monoxide + steam, i.e., with nascent hydrogen.<sup>134</sup> The experiments, conducted at  $400^{\circ}$  in a steel autoclave, demonstrated that the hydrocarbon portion of primary tar, which had previously been distilled at ordinary pressure down to coke, and the hydrocarbon fractions of primary tar thus treated, did not undergo any modification which affected the boiling points. On the other hand, the phenol portion of primary tars, no matter whether treated by itself or in the presence of the hydrocarbons, was converted into oils partially insoluble in alkali.

Phenols boiling below  $250^{\circ}$  proved to be not amenable to hydrogenation under the conditions stated, whilst phenols from primary tar boiling between  $250^{\circ}$  and  $340^{\circ}$  could be hydrogenated under the most diverse experimental conditions. The reaction products had apparently not parted with their oxygen. There had merely been an addition of hydrogen, converting the phenols into hydro-aromatic alcohols, which were thus rendered insoluble in alkali.

### 7. Summary of the Recovery of Light Motor Spirits from Primary Tars

The possibilities of recovering light motor spirits from the primary tars of bituminous and brown coal in the various ways described may be summed up as follows :

#### (a) Low-boiling Constituents of the Gases of Low-temperature Carbonisation.

It has been shown that the gases of low-temperature carbonisation contain benzines. The figures reproduced in Table XLVII were obtained by compressing large volumes of low-temperature carbonisation gas in steel cylinders previously charged with kerosene. The benzine absorbed was subsequently recovered by distillation. At the present time the recovery by means of activated carbon is more convenient and, perhaps, more promising; particularly for the stripping of highly-diluted benzine from producer gas. The proportions of such benzine are considerable; they amount to one-third per cent. of the weight of the coal.

TABLE XLVII

	% by weight of coal.
Low-boiling gas benzine from fat coal (Ruhr) . . . . .	0.17
"      "      "      "      fat coal (Minden) . . . . .	0.3
"      "      "      "      gas flame coal (Lohberg) . . . . .	0.3

#### (b) Alcohol from Low-temperature Carbonisation Gas.

There are other ways of utilising the gases from low-temperature carbonisation for the production of liquid fuels. They contain up to 10 per cent. of ethylene and its homologues. The higher olefines can be absorbed by concentrated sulphuric acid, and subsequently ethylene by chlorosulphonic acid (according to W. Traube, easily and quantitatively); decomposition with water yields the corresponding alcohols.

Table XLVIII gives the amounts of unsaturated compounds in the gas obtained by carbonising the upper portion of the fat coal seams Catharina du Matthias, Preussen I Colliery. Propylene, butylene, and the other homologues of ethylene are almost instantaneously extracted by concentrated sulphuric

TABLE XLVIII

Carbonising stage.	Unsat. compounds sol. in cold conc. $\text{H}_2\text{SO}_4$ . % by vol.	Unsat. compounds insol. in cold conc. $\text{H}_2\text{SO}_4$ but sol. in $\text{SO}_2\text{HCl}$ . % by vol.	Total unsat. compounds. % by vol.
400°	5.6	6.4	12.0
425°	5.6	8.4	14.0
450°	3.2	5.2	8.4
475°	2.0	2.4	4.4

acid in the cold; \* the action of chlorosulphonic acid on ethylene was equally rapid and satisfactory.

(c) *Low-boiling Constituents of Primary Tar.*

It is convenient to speak of tar benzines as distinct from gas benzine. Whether the benzine will be found in the gas or in the tar will mainly depend upon the mode and efficiency of condensation.

The proportions of the more volatile benzines of several low-temperature tars are given in Table XLIX. The tar of the gas flame coal contains up to 10 per cent. of constituents boiling below 200°; as the coal yields about 10 per cent. of primary tar, that figure represents 1 per cent. of tar benzine in coal.

TABLE XLIX

Tar benzine of various primary tars, boiling below 200°.		% of tar.
Gas flame coal	.	10
Rhenish brown coal	.	3.4
Saxon carbonising coal	.	6

(d) *Benzine by Thermal Decomposition of High-boiling Tar Hydrocarbons.*

Prolonged heating of the hydrocarbons of low-temperature tars, especially of those boiling above 300°, to that or a higher temperature, leads by way of molecule scission to the formation of gases and of low-boiling hydrocarbons of the benzine type. A considerable portion of the latter are unsaturated and pass, by absorption of oxygen, or by polymerisation, into resinous products. For many purposes, it is advantageous to operate in such a way as to keep the proportion of unsaturated compounds as low as possible, allowing them to be hydrogenated.

The first three groups of Table L summarise the results of experiments to which W. Schneider submitted a Saxon brown coal tar; various cracking methods were applied. The third group also gives the low-boiling constituents

\* Tropisch and v. Philippovich<sup>135</sup> found later that an 87 per cent. solution of  $\text{H}_2\text{SO}_4$  is most suitable for the absorption of ethylene.

## CONVERSION OF COAL INTO OILS

of the tar before treatment : 0.5 per cent. below 100°; 1.1 per cent. 100° to 150°; and 8.7 per cent., 150° to 200°.

In destructive distillation, and taking the high-boiling portions over at a very slow rate, this tar yielded 7 per cent. of fractions boiling below 150° against 1.6 per cent. before treatment.

When the vapours were passed through a tube heated to 600°, the fraction boiling below 150° amounted to 15 per cent.

Heated several times above 400° in an autoclave, the tar yielded 25 per cent. boiling below 150°. By the third method the proportion of unsaturated compounds was notably lower than by the two first ones.

TABLE L

*Thermal Decomposition of Saxon Brown Coal Primary Tar*  
(Yields in % of Tar.)

Destructive distillation.				
60-100°	2.6	}	7	}
100-150°	4.3			
150-200°	7.1			
14				
Scission at ordinary pressure.				
below 150°			15	}
150-200°			11	
26				
Scission under high pressure.				
	before		after	
below 100°	0.5	11.6	}	25
100-150°	1.1	13.6		
150-200°	8.7	11		
35				
Bergius process with brown coal producer tar.				
	before		after	
below 210°	}	20	25	}
210-300°			39	
above 300°			80	

A comparison of the fractions up to 200° shows a rise from the original of 10 per cent. to 14 per cent. by the first, 26 per cent. by the second and 35 per cent. by the third method.

The fourth group of Table L reproduces the data published by Bergius<sup>131</sup> in his paper on a "New Method for the Working-up of Mineral Oils from Coal." From a brown coal tar he obtained 25 per cent. boiling below 210°. In Table L, the fraction boiling below 200° by the other methods was 14, 26, and even 35 per cent. As regards quantity, the Bergius process gives, there-

fore, no striking result. The advantage of his method may lie in the absence of unsaturated compounds, but this cannot be judged from the data. The fact that Bergius did not obtain more than 25 per cent. (as against 35 per cent.) boiling below 200° may be ascribed either to his use of a tar of less suitable quality, or to the fact that only a single treatment was given.

The first three groups of Table I are an extract of the results of extensive researches conducted by W. Schneider in this Institute some years ago. I now proceed to deal with researches conducted by myself chiefly in conjunction with Hans Schrader and his assistants.

(e) *Benzol and Toluol by Reduction of the Phenols from Primary Tar.*

The chief raw materials so far considered for the production of low-boiling spirits have been the hydrocarbons of the tar and gas of low-temperature carbonisation. The following is a summary of experiments on the reduction of phenols. Table LI shows that both the total phenols of primary tar and their individual fractions can be converted into benzol and toluol by reduction with hydrogen in an iron tube, internally tinned or sulphided as described on p. 117.

TABLE LI  
*Suitability of Different Phenols*

[illegible]

TABLE LII  
Summary of Light Motor Fuels from Gas Coal

	% of	% of tar.	% of coal.
Gas benzine . . . . .			0.25
Tar benzine . . . . .		10	1
Cracking benzine . . . . .	Hydrocarbons 15	8	0.8
Benzol . . . . .	Phenols about 40	20	2.0
Alcohols . . . . .	12 g. from 50 l. primary gas		1.2
Alcohols . . . . .	from cracking gas.	?	?
	Total light motor fuels		5.25

The phenols boiling below  $250^{\circ}$  are most amenable to this treatment, giving a yield of 66 per cent. Much higher yields cannot be expected, because both the oxygen and the methyl groups are split off in the form of water and of methane, as has been pointed out before.

Table LII finally reviews the total yield of light motor fuels obtainable from gas flame coal according to the experience so far gained.

In the last column of the table the yields are referred to the weights of coal, when their values shrink to more modest figures. Taken absolutely, the figures still remain quite considerable, for a ton of coal gives 50 litres of a light motor spirit in addition to semi-coke, gas and the unused portion of tar.

The manufacture of cracked benzines will not be undertaken unless their value exceeds the loss of the corresponding much larger quantity of high-boiling hydrocarbons utilisable as fuel oil. Not allowing for benzine by cracking, a rough estimate shows about 4.4 per cent. referred to the weight of coal, of light motor spirit, and 5 per cent. of hydrocarbons applicable partly as lubricants and partly as fuel oil.

#### 8. *Purification of Primary Tar Oils by Oxidation under Pressure*

Problems of oil refining are important in the petroleum industry as well as in the tar industries, and a good deal has been written on the subject. The chemical treatment with concentrated sulphuric acid and caustic soda is customary both for the removal of resins and of acid constituents. A restriction in the use of chemicals for refining liquid fuels would undoubtedly be desirable. Recent work proves that tar oils, especially the primary tar oils from brown coal, can be refined by oxidation under pressure.<sup>136</sup> An outline of the method and of the chief results will be sufficient in this place; for experimental detail the original paper should be consulted. Brown coal tar was fractionated, and the fractions were subjected to oxidation by compressed air in a steel shaking-autoclave (Fig. 67) at a temperature of  $200^{\circ}$ , and a total pressure of 35 atm. The compressed air entered the autoclave from a steel cylinder, through a reducing valve, and passed out through a vertical cooler. The cooler was made of steel; the condensation could thus take place while the vapours to be condensed and the air were still under pressure, the air leaving through a valve at the top. After a treatment of only  $1\frac{1}{2}$  hours the smell of treated oil underwent a characteristic change, the tar smell giving way to a pleasant odour. Fractional distillation left oxidation products of high molecular weight in the residue. The distillates were of light colour and had no tendency to subsequent darkening when left in the air, as unrefined oils always have. The less stable constituents of the original oils are oxidised and probably polymerised; they certainly have higher boiling points than before, and on distillation remain in the residue. The advantage of pressure oxidation over "blowing" tar, which is likewise an oxidation by air at an elevated temperature, is that the reaction

proceeds more rapidly, the oxygen of the air is better utilised, and there is no loss of oil vapours by entrainment.

The acid constituents of the original oils, otherwise extracted with caustic soda, are considerably reduced in quantity. The phenols are probably oxidised to higher-boiling compounds which remain in the residue. A complete removal

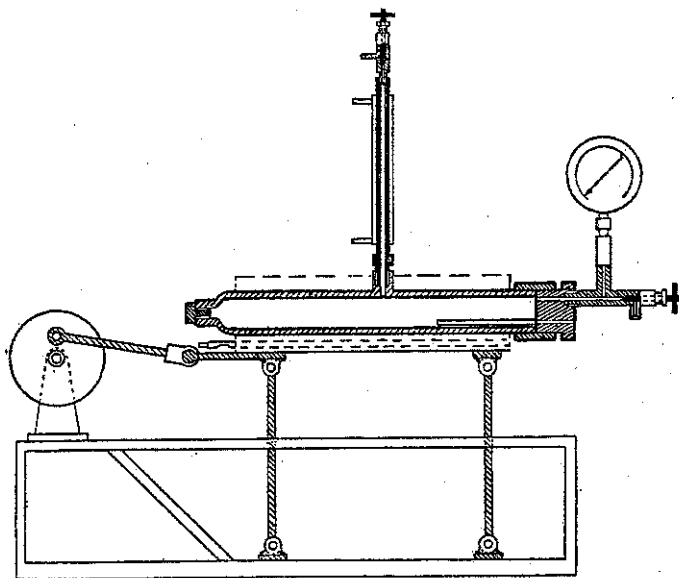


FIG. 67.

of the phenols, however, could not be effected. Before pressure oxidation, the various fractions had the following phenol contents :—

Fraction 150–200°	.	.	.	12 per cent.
„ 220–250°	.	.	.	10 „ „
„ 250–270°	.	.	.	8 „ „
„ 270–300°	.	.	.	5 „ „

After oxidation under pressure, and subsequent distillation from the residues, the percentages of acid constituents were :—

	Soluble in sodium carbonate.	Soluble in sodium hydroxide.
Fraction 150–220° . . . . .	0.8%	3.5%
„ 220–250° . . . . .	1.6%	3.0%
„ 250–270° . . . . .	1.5%	2.0%
„ 270–300° . . . . .	1.8%	3.0%

The reduction in the low-boiling fraction is thus very striking, and points to the commercial applicability of pressure oxidation to the refining of



certain tar oils, especially where the use of chemicals would become too costly.

9. *Formation of Resins and Asphalt from Primary Tar by Oxidation under Pressure*

If oxidation under pressure is continued for several hours, the bulk of the oil is eventually converted into a solid black mass of unknown composition. The formation of resinic and asphaltic solids has been studied in the case of primary tar from bituminous coal both with tar and tar oils,<sup>137</sup> and separately with hydrocarbons and phenols.<sup>138</sup> Phenols pass even more rapidly than hydrocarbons into a solid resinic or asphaltic mass, brown when finely divided and black when fused, which on prolonged oxidation becomes insoluble in all solvents. The liquid hydrocarbons differ somewhat from phenols in this respect, their conversion into similar products being slower and not complete. The solid paraffins of primary tars have been studied more fully;<sup>139</sup> by oxidation under pressure they are converted into higher fatty acids, suitable for soap manufacture and other purposes.

10. *Fatty Acids from Crude Paraffin Wax by Oxidation under Pressure*

The higher fractions of primary tar contain paraffin wax together with viscous oils. Their relative proportions vary within wide limits. In products poor in paraffin wax, which are liquid at ordinary temperature, its presence is indicated only by the high setting point; the corresponding fractions of tar from the carbonisation of brown coal are quite congealed owing to their higher paraffin content. It has been found that crude paraffin wax from primary tar, freed of viscous oils in hydraulic presses, can be converted into fatty acids by oxidation under pressure of air at 170° in the presence of soda lye. Soaps have been prepared in this way in the laboratory.<sup>139</sup> This brief consideration of the oxidation of primary tar and tar oils may suffice for the present purpose.

(s) CONVERSION OF LOW-TEMPERATURE CARBONISATION TAR INTO  
COKE-OVEN TAR

Although this book is intended to deal only with recent processes for the production of oils from coal, and not with the by-products industry of gas works and coke-ovens, which already yield very considerable quantities of liquid fuels, benzol, etc., it appears appropriate to refer to the conversion of low-temperature tar into coke-oven tar in connection with the chapter on the thermal treatment of primary tar. Fractions of coal tar poor in hydrogen (naphthalene) are already being liquefied by hydrogenation, and thus rendered more suitable for power purposes.

Berthelot's old "acetylene hypothesis," which held the field for a long time, explained the formation of the aromatic constituents of coal tar by the primary

generation of acetylene in the retort, and the subsequent polymerisation of acetylene into benzene ( $3C_2H_2 = 3C_6H_6$ ) and its derivatives. A discussion of this hypothesis is hardly called for any more; it has been discarded, in the first instance because the temperatures in the coke-oven or gas-retort are not sufficiently high to lead to an appreciable formation of acetylene, and further because Amé Pictet<sup>7</sup> showed that vacuum tar from coal, a preliminary stage in the formation of low-temperature tar, can be easily converted into an ordinary coal tar by superheating. Pictet passed vacuum tar vapours through an iron pipe heated to a bright red heat which was filled with small pieces of coke. He obtained from 150 to 200 litres of gas per kg. of vacuum tar which had the smell of coal tar, and consisted essentially of hydrogen and saturated hydrocarbons of the methane series with a small proportion of ethylene. The resulting tar smelled like ordinary coal tar; the presence of benzene, naphthalene and anthracene was easily established. This was definite proof that the well-known constituents of coal tar are secondary, and not direct, products of the destructive distillation of coal.

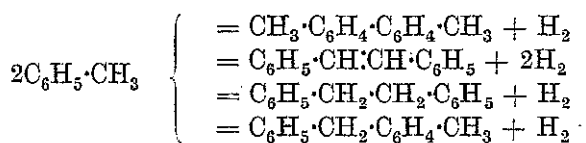
D. T. Jones<sup>140</sup> concluded from his investigations that the formation of coal tar from vacuum tar was essentially due to the decomposition of the naphthenes, paraffins and unsaturated hydrocarbons forming olefines of various carbon content which condense at higher temperature to aromatic substances. Jones observed that the higher (gaseous) olefines are at a maximum at  $550^\circ$ , the curve descending to a minimum at  $750^\circ$ , when they virtually disappear. Their disappearance at  $750^\circ$  synchronises with the appearance of naphthalene, and immediately precedes a rapid increase in the evolution of hydrogen. Hydrogen is formed at middle temperatures, chiefly as the result of the decomposition of naphthenes. The increase at higher temperature must probably be attributed to the union of aromatic molecules and to intramolecular ring-closing. Jones further suggests that benzene and its homologues are chiefly formed as the result of olefinic condensation. To some extent they are secondary products of coal distillation, having been formed by the thermal dehydrogenation of the corresponding naphthenes.

The latter suggestion of Jones may be accepted unconditionally. That the bulk of benzene and its homologues has been formed in another way, *i.e.*, by the reduction of phenols, has meanwhile been established by other investigators.<sup>141</sup> Although the conditions prevailing in the coke-oven are not as favourable as those in the tinned iron tube (see p. 117) for a quantitative reduction of the phenols, they are sufficiently so to explain the formation of all benzene usually produced in practice. For it has been shown that as much as half or one-third of the theoretical benzene yield can be obtained when the reduction takes place under the most unfavourable conditions. The deposition of carbon observed in this case takes place also in the coke-oven, and part of this carbon is found in the tar.

All intermediate stages between primary tar and high-temperature tar are occasionally met with in industrial practice. The liability of primary tar to change, even at 300°, is shown in ordinary distillation, when the most viscous constituents are decomposed into light oils, gas and coke. That these constituents can be isolated at all in the distillation of coal is due to their being diluted by other more stable volatile compounds, and above all to their rapid discharge from the retort or rotating drum. Duration of the reaction and dilution exert an important influence upon the course of the reaction at a given temperature. The dehydrogenation of hydro-aromatic constituents and cracking probably begin at about 500°. The reduction of phenols to benzene and its homologues does not set in below 700°; any benzene hydrocarbons produced at lower temperature are therefore of different origin. A study of the products which have not yet appeared at 500°, and which disappear again at very high temperatures, should prove full of interest. The appearance of carbolic acid and acetone, which are not present in normal primary tar, is probably a case in point.

As has been shown in a previous section, a primary tar, not superheated, contains only a negligible quantity of carbolic acid. Phenol itself, therefore, cannot be the only source of the much larger quantity of benzene in coal tar, which, as has actually been proved, is chiefly derived from cresols and xylenols by simultaneous reduction and demethylation with the formation of water and methane. The term "simultaneous" should not be taken too literally. It would appear that toluene is formed more readily from cresols, and benzene secondarily from toluene. The benzene resulting from this reduction frequently contains 20 per cent. of toluene, whilst a benzene containing appreciable quantities of carbolic acid has never been observed, which should be the case if carbolic acid were first produced by demethylation, and benzene afterwards by reduction. It may be possible to select conditions in which demethylation takes place in the first instance, which would be important for the production of carbolic acid.

If we assume the reduction of xylenol to xylene to be completed, the further action of hydrogen would, according to present views, lead to the formation of toluene and methane. The formation of benzene would then follow with renewed evolution of methane. It has been shown <sup>142</sup> that toluene, at high temperature and in the absence of hydrogen, will split off hydrogen and then pass into larger molecules of dibenzyl, stilbene, ditolyl and *p*-methyl-diphenylmethane, as indicated below.



In the case of benzene, the reaction  $2\text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{H}_2$  proceeds similarly, from left to right when there is a deficiency of hydrogen, and from right to left when hydrogen is in excess. The formation from phenol of a large number of solid compounds in coal tar can thus be explained, but that of naphthalene is not yet certain. Part of the naphthalene in coal tar is no doubt formed from methyl-naphthalene, or by simultaneous dehydrogenation and demethylation of the hydrogenated methyl-naphthalenes of primary tar. Another portion is probably of thermal origin, and must be considered as a very stable final product of condensation and dehydrogenation processes acting on benzene and its homologues, as must also be anthracene.

#### (t) CONVERSION OF BROWN COAL TAR INTO AROMATIC TAR

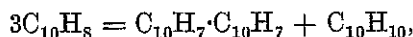
So far as can be judged at present, the primary tars from brown coal and bituminous coal differ mainly in the proportions of the various types of constituents. The Montan wax of brown coal consists of waxes and resins. The composition of the waxes is fairly well understood. They consist of the esters of higher fatty acids ( $\text{C}_{25}, \text{C}_{27}, \text{C}_{29}$ )<sup>143</sup> with high alcohols ( $\text{C}_{34}, \text{C}_{26}, \text{C}_{30}$ ).<sup>144</sup> and of an excess of free fatty acid of high molecular weight. Whilst the fatty acids in the carbonisation of brown coal are converted via ketones into the corresponding paraffins, carbon dioxide being split off, the alcohols conceivably form olefines with liberation of water, or naphthenes by the closing of rings. Primary brown coal tar also contains phenols, largely derived from ulmins, the main constituents of coal. In brown coals rich in wax, the ulmic constituents are relatively less predominant; tar from such coals, therefore, contains more decomposition products of Montan wax and less phenols. In general, a tar from rich brown coal differs from that of good bituminous coal by its high content of paraffin wax and its low percentage of phenolic components.

The liability of primary brown coal tar to decomposition in ordinary distillation, and its behaviour on cracking under pressure, have been mentioned before. Its behaviour at about  $700^\circ$  was investigated by Liebermann and Burg<sup>114</sup> as early as 1878. It was then found that the fractions  $200^\circ$  to  $300^\circ$  of a brown coal tar oil, mainly consisting of hydrocarbons, contained only 4 per cent. of benzene after passage of the oil through an iron tube charged with pieces of wood charcoal at bright red heat. In explanation, Salzmann and Wichelhaus<sup>115</sup> suggested that, in the formation of products richer in carbon and poorer in hydrogen than the raw material, the vapours took up carbon from the incandescent charcoal, or that hydrogen was liberated, or that the molecules of vapour were dissociated into molecules of high and of low hydrogen percentages, benzene being one of the latter products. To-day we know that none of the three assumptions can be maintained, but that the bulk

of benzene is a reduction product of phenol. A primitive conversion of brown coal tar oils into coal tar-like products has thus long been known, but by selecting working conditions with present-day knowledge much better results should now be realisable, as they are in the case of the hydrogenation of petroleum (*Brennstoff-Chemie*, 1923, 4, 201).

(u) LIQUID MOTOR FUELS BY HYDROGENATION OF COAL TAR, AND  
ESPECIALLY OF NAPHTHALENE

Modern methods applied in gas works and in coke-oven plants have become more and more alike. In recognition of the fact that the production of a good coke is of great economic importance, a number of gas works have even been fitted out with coke-oven plant. The manufacture of a firm coke calls generally for rapid heating by plunging the coal into incandescent chambers. Primary tar is not obtainable under these conditions; in its place appears coke-oven or gas tar in much smaller quantity and with a naphthalene content increasing with the temperature used. Owing to its ready crystallisation, naphthalene is one of the few products of coal tar which can be easily isolated and purified by pressing, recrystallisation and sublimation. Its annual production is very considerable, and its suitable utilisation has long been a problem of some importance. At one period naphthalene was used as a cheap motor fuel. One of the drawbacks attaching to its use was that it had to be melted and fed into the engine through heated pipes. It was, therefore, desirable to convert the solid naphthalene into a liquid fuel. It was found that purified naphthalene on heating in an autoclave with 4 per cent. of aluminium chloride at a pressure of 10 atm. undergoes, in less than half an hour, a change, so that it yields from 30 to 40 per cent. of a liquid product.<sup>145</sup> The aluminium chloride seems to act in this reaction as a hydrogen carrier, one part being hydrogenated, and another dehydrogenated and condensed. The reaction may be expressed by the equation:—



the products being di-naphthyl and di-hydronaphthalene. The liberation and addition of hydrogen is, however, not limited to the formation of these two products, but leads to derivatives either richer or poorer in hydrogen. Partial liquefaction of naphthalene was superseded by the tetralin process.

Sabatier and Senderens had shown that naphthalene vapour passed over finely divided nickel at 200°, in the presence of an excess of hydrogen, is transformed into tetra-hydronaphthalene (b. p. 205°). At 175°, deca-hydronaphthalene (b. p. 187°) is the hydrogenated product (Sabatier, "Catalysis"). Schroeter<sup>146</sup> modified the process on the lines of the fat-hardening method by working with the liquid material and hydrogen under pressure, in the presence of nickel. The technical application of this obvious proposal was rendered very

difficult by the sulphur compounds in commercial naphthalene, which rapidly poison the catalyst. Those difficulties were eventually overcome by a preliminary purification. The elimination of the last traces of sulphur by means of sodium, and the reduction of the sodium consumption to economic limits, made manufacture on a very large scale possible.

To-day, according to this method, a number of other hydrogenated products are manufactured on a large scale at suitable temperatures and hydrogen pressures, among these being tetra-hydronaphthalene (tetralin), deca-hydronaphthalene (decalin) and various derivatives of benzene, phenol and their homologues.

That a purification by the aid of sodium, and consequently the catalytic hydrogenation with nickel as catalyst, is commercially impracticable in the case of tar and tar oils has already been stated. These materials may be submitted to Berginisation. The following is an extract from the Patent Specification dealing with this invention.

*Bergius' Brit. Pat. No. 5021 of 31 March, 1915 (date of application in Germany, 2 April, 1914)*

" This invention is an improvement in or modification of that described in Specification No. 18,232 of 1914. In carrying out the process according to the prior specification with pressures of more than 20 atmospheres, it has been found that the hydrogenating reaction can be effected not only with coal and other solid carbonaceous material of vegetable origin, formed by natural or artificial carbonisation, but with certain products of distillation of coal and of the said other carbonaceous materials, such as tar and pitch and other solid or liquid carbon compound obtained by distillation. It is possible to convert tar by heating it with compressed hydrogen of more than 20 atmospheres to temperatures of about 400° C. into a fairly thin fluid, from which hydrocarbons having properties similar to those of rock oil hydrocarbons can be separated by distillation.

" The process is applicable to solid and liquid hydrocarbon containing products of destructive distillation of coal and other solid carbonaceous material of vegetable origin formed by natural or artificial carbonisation, obtained at high temperatures in coking and gas retorts.

#### EXAMPLE

" One kg. of tar is heated with hydrogen at 100 atmospheres pressure to 400° C. in an autoclave. After 4 hours, the mass is distilled off. Sixty per cent. of tar is distilled at about 250° C. and can be further treated by rectification.

" Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is :

"A process of manufacturing liquid organic compounds as set forth in Specification No. 18,232 of 1914, applied to the solid or liquid products of destructive distillation at the high temperatures of coking and gas retorts of coal or other substances produced by natural or artificial carbonisation of vegetable matter and carried through at pressures of more than 20 atmospheres."

The following details of an experiment of this kind may be quoted.<sup>147</sup> Gas works coal tar was freed of its constituents boiling below 230°. It was then charged into an autoclave together with its own weight of pebbles and 5 per cent. of iron oxide; hydrogen was forced in under pressure of 50 atm., and the contents were stirred. The temperature was raised to 480°, and then kept constant until there was no further drop of pressure. After cooling, the pressure was 32 atm. It was raised again to 50 atm. by replenishing the hydrogen, and heating to 480° was repeated until the pressure reduction had ceased once more. After cooling, a gas pressure of 30 atm. was observed. There had thus been a total pressure loss of  $18 + 11 = 29$  atm., which would, in the autoclave of 5 litres capacity, correspond to a consumption of  $4.4 \times 29 = 128$  litres of hydrogen, making due allowance for the volume of the charge. The density of the tar, originally 1.144 at 15°, had been reduced by hydrogenation to 1.041; 33 per cent. of the reaction product boiled below 230°, and another 33 per cent. between 230° and 330°.

Part of the combined carbon of the original tar was, after the experiment, in the gas, of which 140 litres were blown off. It contained only 48 per cent. of hydrogen, and 39.6 per cent. of methane and its homologues. That would mean a certain loss, but the gas can be readily used like ordinary coal gas, being similar in composition. The original tar had an ultimate composition: carbon 87.56 per cent., hydrogen 6.04 per cent.; the composition of the Berginised product was:—

	Carbon.	Hydrogen.
Fraction below 170° . . .	83.48%	11.26%
„ 170–230° . . .	85.09%	8.56%
„ 230–330° . . .	88.98%	7.31%

The figures prove that, in the hydrogenation of tar oils, Berginisation can indeed replace the tetralin process which cannot be applied to these for obtaining products of lower boiling points from higher-boiling compounds. In view of the high temperature of 480°, hydrogenation, presumably, cannot be pushed above certain limits, unless pressures of several hundred atmospheres are available. It has been shown that the Berginisation of primary brown coal tar does not give larger yields of benzine than cracking under pressure and

without hydrogen. This may be explained by the fact that the material treated was much richer in hydrogen than gas works' tar, and that, for this reason, hydrogenation soon came to a standstill. That view would dispose of the apparent contradiction in the facts that hydrogenation of the high-boiling fractions of gas works' tar was successful, whilst the same process did not, as regards yields of low-boiling constituents, offer any advantage over cracking under pressure when applied to brown coal tar, though it yielded better and less unsaturated products. This argument is supported by Waterman's experiments with paraffin wax.

#### (v) IMPORTANCE OF PRIMARY TAR AS RAW MATERIAL

In concluding the principal chapter of this book, which was devoted to the production of primary tar, with a discussion of its working-up, I should like briefly to give my reasons for the importance which I attach to the production of primary tar and to the knowledge at least of some classes of the bodies \* contained in it. Primary tar must be regarded as a raw material, and not as a finished product of manufacture. By selection and invention of suitable methods it can be worked-up into valuable products, light and heavy liquid fuel and lubricants. By appropriate thermal treatment, primary tar, if it does not contain products utilisable in the chemical industry, will give the known coal tar products in higher purity and better yield, because the temperature of decomposition can be controlled at will and is not fixed by the requirements of the coke-oven or gas retort. Systematic thermal treatment of primary tar is bound to produce results of value to the chemical industry, as is indicated by the formation of carbolic acid and acetone under certain conditions.

For those reasons it appears perfectly justifiable to recover from coal before it is used for other purposes the most primary kind of tar which at the same time represents the highest possible yield.

The residue of carbonisation is, by one of the most interesting modes of application, converted into Synthol (Chapter IV); water gas is made from semi-coke and subsequently transformed into motor fuel by a contact process on the lines of Haber's ammonia synthesis. Primary tar treatment which yields chiefly heavy fuels, and the Synthol process which converts the semi-coke into light fuels, would supplement one another in a most fortunate sequence of manufactures, leaving behind nothing but the mineral constituents of coal.

\* The isolation of individual compounds is of no value for the knowledge of primary tar, as long as their quantitative relationship is not definitely known and if there is no definite proof that the product examined is in fact a primary tar and not a product of superheating it.



## CHAPTER III

### HYDROGENATION OF COAL

#### (a) BY MEANS OF HYDRIODIC ACID UNDER PRESSURE ACCORDING TO BERTHELOT

MORE than fifty years ago Berthelot <sup>148</sup> first succeeded in converting natural coal into oils by hydrogenation. For this purpose he treated coal with about 100 parts of saturated hydriodic acid at 270° for about 24 hours. He described his experiments as follows: "I experimented with coal purchased from the 'Compagnie Parisienne.' The exact source was not known, but the coal was of a type which yielded 4 to 5 per cent. of tar. I collected the gas and liquor, and determined the iodine quantitatively. The residue was an agglomerate resembling bitumen, and represented a little more than one-third of the weight of the coal. The iodine liberated amounted to twelve times the weight of coal; the gases consisted mainly of hydrogen. The liquids amounted to 60 per cent. of the weight of coal, that is, their weight was twelve to fifteen times greater than that of the tar which this coal could have furnished; this is sufficient proof that the new hydrocarbons were derived from the coal substance. The liquids were submitted to two series of fractional distillation. I first isolated a small quantity of hexane,  $C_6H_{14}$ , boiling at about 70°; this hexane contained a little benzene, which I converted into nitrobenzene, aniline, etc. After the hexane, several hydrocarbons came over which showed the general properties of saturated hydrocarbons; the mixture was too complex to admit of accurate separation. The last products, still abundant, were oily."

Of Berthelot's further experiments on the liquefaction of solid fuels, the hydrogenation of a very young fuel, viz., wood, and further, charcoal and carbon itself, may be referred to.

"*Wood.*—Wood consists of various insoluble compounds which, in the main, may be regarded as sugar derivatives formed by gradual combination and molecular condensation. I made use of the wood of matches, and took the precaution to split it into thin splinters and to dry it. In contact with hydriodic acid, the wood blackened at once. I heated part of the substance with 80 parts of saturated acid for 24 hours to 280°. Apart from a trace of carbon, the wood was almost completely transformed into liquid hydrocarbons, which represented about two-thirds of the weight of wood used. The hydrogen liberated was measured; it contained only a small quantity of hydrocarbon vapours. If from the weight of iodine liberated (which was determined experimentally) the weight of iodine equivalent to the volume of hydrogen is deducted, there remain 1100 parts of iodine set free by the hydrogenation of 100 parts of wood, corresponding to 8.6 parts of hydrogen. I shall revert to

this figure. The liquid hydrocarbons were fractionated by two series of distillations, which yielded :

(1) Hexane,  $C_6H_{14}$ , boiling about  $70^\circ$ , produced in appreciable quantity. It did not contain any benzene, and gave the usual reaction of methane hydrocarbons.

(2) Dodecane,  $C_{12}H_{26}$ , boiling about  $200^\circ$ , and amounting to about half of the product. It was analysed; it resisted the action of bromine, fuming nitric acid, fuming sulphuric acid, etc.

(3) An oily hydrocarbon of the methane series, of equal stability, but volatile at a high temperature, of composition  $C_{24}H_{50}$ .

"The formation of these hydrocarbons agrees with the composition of the principal proximate components of wood; their carbon is a multiple of six atoms, as that of the sugars and their derivatives. It also agrees with the amount of hydrogen fixed in the hydrogenation of wood. The wood used contained in the dry state :

Carbon . . . . .	49.0 per cent.
Hydrogen . . . . .	6.0     "
Oxygen . . . . .	43.0     "
Ash . . . . .	2.0     "

"To convert 43 parts of oxygen into water requires 5.4 parts of hydrogen. If it is assumed, on the other hand, that 49 parts of carbon have been converted into one hydrocarbon  $C_{12}H_{26}$ , the predominant product of the reaction the formula of which corresponds with the mean composition of the mixture of hydrocarbons obtained, then 8.9 parts of hydrogen are required, a figure agreeing with the iodine liberated. Altogether  $5.4 + 8.9 = 14.3$  parts of hydrogen are required to convert 100 parts of wood into saturated hydrocarbons. The wood contained already 6.0 parts of hydrogen, and it absorbs 8.6 parts, giving a total of 14.6 parts in agreement with the previous value.

"*Charcoal*.—I selected fragments, well carbonised to the core, of a very light and porous charcoal (Charbon de fusain) such as artists use for sketching. The high porosity of this material, and the relatively low temperature at which it had been made, seemed to make it most suitable for my purpose. This material is known to contain considerable quantities of hydrogen and oxygen. One part of this charcoal was heated to  $280^\circ$  with 100 parts of hydriodic acid. The gases and liquids were collected, and the iodine was estimated quantitatively. About one-third of the charcoal had resisted the attack, or to be more correct was changed into a lumpy, bitumen-like mass, richer in hydrogen. The gas was hydrogen mixed with a small quantity of a highly volatile hydro-

carbon. The liquids, which amounted to 70 per cent. of the original coal, were fractionated twice, and I isolated :

(1) Hexane,  $C_6H_{14}$ , in small quantity, boiling at about  $70^\circ$ , showing the characteristic properties of this body.

(2) Dodecane,  $C_{12}H_{26}$ , the chief product, boiling at about  $200^\circ$ , of the composition and properties stated above.

(3) An oily, almost solid, hydrocarbon, about one-third of the product, giving the reactions of methane hydrocarbons. It is probably the hydrocarbon  $C_{24}H_{50}$ .

" By deducting from the weight of the iodine obtained that corresponding to the gas, I found that 100 parts of drawing charcoal had, by its hydrogenation, liberated 1270 parts of iodine. The weight of iodine equivalent to that of the hydriodic acid required for complete hydrogenation of 100 parts of charcoal would be about 1410 parts. As stated, about one-third of the charcoal had been merely transformed into a bituminous mass; there is, therefore, no discrepancy between the results obtained and the theory.

" It should be noted that the hydrocarbons yielded by charcoal are identical with those from wood; this shows that even so violent a reaction as charring does not completely destroy the chemical structure of the proximate constituents of wood. In other words, the compounds contained in wood still represent certain condensed derivatives of the compounds, *i.e.*, the sugars, contained in wood. I shall presently show that, up to a point, the same conclusion holds good for pure carbon, if it is derived from charcoal.

" *Pure Carbon.*—When charcoal is submitted to progressively intensified calcination, it is less and less attacked by hydriodic acid as it approaches the state of pure carbon. Coke is no longer attacked by this reagent, nor is natural graphite. The carbon produced by the decomposition of sodium carbonate with phosphorus at red heat resists the reaction, as does the carbonaceous matter which results from the treatment of aromatic compounds at  $280^\circ$  with an insufficient amount of hydriodic acid. (Berthelot, *Les carbures d'hydrogène*, III, pp. 144, 146, 147). The charcoal ceases altogether to be attacked by hydriodic acid if it is completely deprived of its hydrogen, which can be effected by the action of chlorine at red heat. Yet the carbon derived from charcoal and other organic compounds retains some trace of its origin, and of its chemical as well as physical structure. I have indeed succeeded, by the aid of the two following wet reactions, in transforming pure carbon into hydrocarbons.

" I have observed that pure carbon, as prepared by the action of chlorine on artists' charcoal at red heat, has the property of being slowly dissolved by nitric acid at  $80^\circ$ . A brown soluble substance is formed which I have so far not been able to convert into any known organic compound. Hydriodic acid

had the desired effect. Under the conditions described, it converted the compound at  $280^{\circ}$  into methane hydrocarbons,  $C_nH_{2n+2}$ , similar to those obtained from wood. Owing to scarcity of material I could not study these compounds in detail, but characterised them in a general way. This experiment is, I believe, the first example of the formation, below  $300^{\circ}$  and in an aqueous medium, of a hydrocarbon from pure carbon. The experiment shows that pure carbon retains something of the organic structure of the bodies from which it was produced, and of which it represents a derivative defined by molecular condensation."

The experiments of Berthelot make it clear that his hydrogenation is only successful if carbon is treated, not as such, but in form of carbon compounds, such as wood or coal, or partially calcined charcoal. That coal, in spite of its high carbon percentage, does not contain free carbon, but only highly carbonaceous compounds, is evident from the fact that free carbon has never been observed on treatment with a variety of solvents. Further, coal, but not carbon, can be easily oxidised by means of ozone to compounds soluble in water. The possibility of Berthelot's intensive hydrogenation also supports this view. He was only able to hydrogenate carbon itself after converting it by oxidation into compounds. Hydrogenation offered no difficulties in the case of lightly calcined charcoal; this is easily understood, for by determining the electrical conductivity it has been found that charcoal must be heated to  $700^{\circ}$  before it loses sufficient hydrogen to form practically free carbon.<sup>149</sup>

(b) COMPARATIVE HYDROGENATION OF DIFFERENT COALS WITH HYDRIODIC ACID

The experiments of Berthelot were extended by Tropsch,<sup>150</sup> who investigated the hydrogenation of coals of different geological ages with the aid of hydriodic acid and phosphorus. He did not succeed in liquefying coal completely, but was able to show that the solubility of hydrogenated coal in chloroform was greater the younger the coal. This solubility in chloroform before and after hydrogenation is given in his laboratory notes as follows :

1. *Anthracite, Gottfried Wilhelm Colliery, Mausegatt Seam (Coke yield 89 per cent.)*

0.52 per cent. of chloroform extract was obtained from anthracite. Two grams of anthracite were mixed with 2 grams of red phosphorus, and were heated with 5 c.c. of hydriodic acid of spec. grav. 1.7 in a sealed tube for 12 hours to  $200^{\circ}$ . There was gas pressure in the cooled tube. The contents were diluted with water and filtered. A black, sandy product of the reaction remained on the filter which did not differ in appearance from anthracite; but the phosphorus had disappeared. The product was exhaustively extracted

with chloroform, the extract was evaporated, and the residue heated in a vacuum on the water bath until the weight remained constant. 0.243 gram of extract was obtained, representing 12.1 per cent. of the weight of the anthracite.

2. *Semi-bituminous Coals (Esskohle), Rosenblumendelle Colliery, Girondelle Seam (Coke yield 85 per cent.)*

Chloroform extract 0.55 per cent.

Two tubes, each charged with 0.8 gram of coal, 0.8 gram of red phosphorus and 3 c.c. of hydriodic acid (1.7 spec. grav.), were heated to 200° for 12 hours and treated as described. The filter residue was washed with bisulphite to remove iodine. The product again did not much differ from the original coal; but the phosphorus had disappeared. Extraction of the dried residue with chloroform gave 0.2826 gram of extract, 17.7 per cent. of the coal.

3. *Fat Coal, Osterfeld Colliery, Albert Seam (Coke yield 78 per cent.)*

Chloroform extract 0.71 per cent.

The quantities used and treatment were as in 2. The product was a scaly black mass which was filtered, washed with bisulphite, dried and extracted with chloroform. The residue gave 0.8732 gram of extract, 54.6 per cent. of the coal.

4. *Gas Flame Coal, Bismarck Colliery (Coke Yield 64 per cent.)*

Chloroform extract 1.5 per cent.

Quantities used and treatment as in 2 and 3. After heating, the content caked; it was fused by means of warm water, powdered after cooling, washed with bisulphite and dried, giving 1.124 grams of extract, 70.3 per cent. of the coal.

By a modification of Berthelot's process, we succeeded eventually in obtaining liquids of hydrocarbon character by heating the coal with hydriodic acid and phosphorus to 280°. For 0.5 gram of extracted gas flame coal (Rheinbaben Pits), 1 gram of red phosphorus and 10 c.c. of hydriodic acid (spec. grav. 1.7) were used. On account of the high pressure we heated the sealed tube in a steel tube, half filled with water so as to equalise the pressure. After 6 hours the reaction was completed and the phosphorus had disappeared. Droplets of oil, coloured by free iodine, floated on the hydriodic acid. After adding sulphurous acid, and steam distillation, about 30 per cent. (of the weight of coal) of a colourless petroleum-like liquid was obtained; the non-volatile residue was a bituminous mass, mostly soluble in chloroform.

The discrepancy between our results and Berthelot's may be due to the different coals used, although other unknown factors may play a part in the reaction.

*Brown Coal.*—We then studied the action of hydriodic acid and phosphorus on brown coal. The brown coal came from the Riebeck Montan Works, and gave on carbonisation 48.3 per cent. of coke, 17.3 per cent. of tar and 10.0 per cent. of liquor, all related to coal dried at 105°. 18.2 per cent. of bitumen could be extracted from it with benzene. We used coal extracted with benzene under pressure.

Three tubes, each containing 1.2 grams of brown coal, 1.2 grams of red phosphorus and 5 c.c. of hydriodic acid (spec. grav. 1.7) were heated to 200° for 12 hours. The product of reaction was a soft brown mass, which on steam distillation gave a small amount of an oily liquid and some iodine. The distillation residue solidified to a brittle yellow-brown mass, from which chloroform extracted 2.17 grams, or 60 per cent., leaving a light yellow substance behind. The chloroform extract had about the same properties as the products obtained from bituminous coal under equal conditions.

The experiments described proved that hydrogenation of coal by means of hydriodic acid can be effected more easily the younger the coal. Hydrogenation is also successful with brown coal, and its resulting products resemble those from bituminous coal. Whilst at 200° the products obtained are bitumen-like, of high molecular weight and soluble in chloroform, working under special conditions and at higher temperatures yields liquids of petroleum character. Instead of hydriodic acid which Berthelot, and after him, Tropsch, had used in their hydrogenation experiments, Fischer and Schrader<sup>151</sup> first tried sodium formate, which, on heating, readily liberates hydrogen, and later a mixture of carbon monoxide and steam, which yields hydrogen at high temperature. Whether in these two cases hydrogen was actually liberated in the first instance, or whether formic acid, present or formed, acted as hydrogen carrier, remains as yet undecided.

### (c) HYDROGENATION BY MEANS OF SODIUM FORMATE

The autoclaves used in the experiments with formate, and subsequently with carbon monoxide as hydrogenating agent, were of the type of the apparatus illustrated in Fig. 68. They were drilled out of a block of Siemens-Martin steel, and the same drill conveniently served later to remove the reaction products completely from the cylinder. The autoclave<sup>152</sup> was closed, as in previous cases, with the aid of a sleeve with left and right-handed thread pressing the head against the cylindrical body. The joint was made either by means of the conical seat shown in the diagram, or of a collar and groove into which a ring of copper or iron was fitted. For the purpose of charging the cylinder with compressed gases and releasing them, a valve was provided in the head. The spindle of this valve was made very long; the passage leading from the small opening in the interior of the autoclave could thus be kept very short, and any products condensed in this part would offer little resistance to

the escape of the gases. The upper portion of the cylinder was filled up with an iron piston so as to place the heated reaction chamber in the lower part of the apparatus. Thus, the surface of the joint was not exposed to the high temperatures. A thermometer or thermo-couple was inserted into a hole drilled through the cover and wall of the cylinder. The dimensions adopted admitted of heating up to  $450^{\circ}$ , at pressures of several hundred atmospheres.

The electric furnace used for heating the autoclaves consisted of an iron tube wound with iron wire on asbestos lagging; the tube was placed vertically in a box filled with sand to the upper edge of the pipe. The lower edge of the sleeve of the autoclave rested on the furnace tube. Long wires connected the thermo-couple with a millivolt meter mounted in a shelter at a safe distance. Two blank experiments, made to show the behaviour of coal without an addition of formate, gave the results tabulated in Table LIII. Heated in the autoclave without water, the coal yielded 1.3 per cent. of ether-soluble products; with twice the weight of water, the yield rose to 10.1 per cent. of the coal substance.

Expt. 1, Table LIV, shows that in the presence of formate, but without water, the oil yield was 44 per cent. against 1.3 per cent. in Expt. 1, of Table LIII. With addition of water in the presence of formate in Expt. 2, Table LIV, no further increase in the yield was observed.

The material used was 4 grams of powdered Union briquettes, containing 3.16 grams of ash-free dry coal and 8 grams of sodium formate. In the experiment without water an intimate mixture was obtained by evaporating the formate solution stirred into the coal. The iron autoclave, 31 c.c. capacity, was heated to  $400^{\circ}$  for 3 hours, after which there was a moderate gas pressure. The oil formed was taken up with ether, and the solution which showed intense yellow-green fluorescence was dried with sodium sulphate, and evaporated. A mass of ointment consistency, reddish-brown in thin layers, and

smelling of tar was obtained. The residue, insoluble in water and ether, was collected on a filter and dried at  $105^{\circ}$ . The residue from the experiment without water was brownish-black, and yielded, on heating, a further fairly large amount of pasty tar; whilst the residue from the experiments in presence of water was a light yellow-brown powder, and nothing but the ash appeared

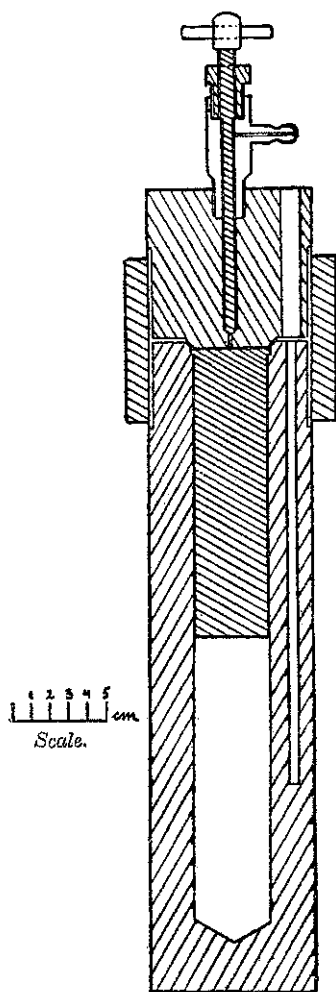


FIG. 68.

TABLE LIII

Heating 4 grams brown coal\* (Union briquettes) under pressure for three hours at 400° in autoclave of 31 c.c. capacity without addition of formate.

Expt. No.	Addition.	Ether soluble.		Residue. g.
		g.	% of ash-free dry coal.	
1	no water	0.04	1.3	2.04
2	8 c.c. „	0.32	10.1	1.73

TABLE LIV

*Influence of Water* *NaCHO<sub>2</sub>*

4 grams brown coal (Union briquettes) and 8 grams sodium formate heated for 3 hours at 400° in autoclave of 31 c.c. capacity.†

Expt. No.	Ash-free dry coal used. g.	Water present. c.c.	Ether soluble.		Residue. g.
			g.	% of ash-free dry coal used.	
1	3.16	—	1.39	44.0	0.87
2	3.16	8	1.42	44.9	0.53

to remain. It still contained some organic substance, however, and when heated turned black and gave a little oil.

The hydrogenation experiments summarised in Table LV give a further proof that the presence of water does not increase the oil yield. The sodium formate employed in these experiments was not the pure salt used in the first series, but a 91.5 per cent. preparation. Here, again, the presence or absence of water made little difference in the oil yield.

The superior results realised with formate must, therefore, be ascribed not to the presence of the water, but to the hydrogen and carbon monoxide generated by the decomposition of formate, and compressed. This point will be discussed below. The favourable effect might be due to the slower decomposition of the formate under pressure, so that the nascent hydrogen is not liberated faster than it can combine with the coal.

\* The ether extract from untreated Rhenish brown coal was 1.6 per cent., the montan wax extracted with benzene in a Soxhlet was 3.5 per cent.

† This autoclave was not yet provided with the valve described on p. 179, hence the gases formed could not be measured,



TABLE LV

*Hydrogenation of Brown Coal (Union Briquettes) with Commercial Sodium Formate (91.5 per. cent.)*

75 grams brown coal heated to 400° with 75 or 150 grams sodium formate for 3 hours in autoclave of 255 c.c. capacity.

Expt. No.	Formate used. g.	Water used. c.c.	Gas formed. l.	CO <sub>2</sub> formed. l.	Oil volatile in steam. c.c.	Ether soluble part of solid product.		Carbonaceous residue.		Formate left over g.
						g.	% of ash-free dry coal.	g.	% of dry coal used.	
1	75	—	13.75	4.02	0.4	17.9	30.2	25.9	41.3	5.27
2	75	25	14.42	6.22	0.3	16.5	27.8	30.0	47.8	0.3
3	75	75	8.94	3.29	0.3	15.5	26.2	30.7	49.0	0.5
4	150	50	12.82	4.10	0.1	14.5	24.4	33.4	53.2	0.52
5*	150	50	8.81	3.22	—	18.2	30.7	30.0	47.8	0.26

\* Heated for 6 hours.

*Influence of Temperature upon the Hydrogenation of Brown Coal*

The experiments with brown coal (Union briquettes) at 400° were supplemented by two further trials at 350° and 450°, details of which are given in Table LVI.

TABLE LVI

4 grams brown coal, 8 grams sodium formate, 8 c.c. water heated for 3 hours in iron autoclave of 31 c.c. capacity.

Temp.	Ether-soluble.		Residue.			
	g.	% of ash-free dry coal.	Total. g.	Ash content. g.	Organic substance.	
					g.	% of ash-free dry coal.
350°	0.91	28.8	1.27	0.25	1.02	32.28
400°	1.42	44.9	0.53	0.32	0.21	6.64
450°	0.25	7.9	0.59	0.21	0.38	12.02

The maximum yield of substances soluble in ether was therefore obtained at 400°; at 350°, the yield decreased to 64 per cent.; at 450°, to 18 per cent. of the maximum.

At 350°, the ether-soluble portion was a reddish-brown, highly viscid mass. The dark-brown coal residue intumesced strongly on heating, and liberated gas, but hardly any tar. At 400°, the ether extract was of pasty consistency,

TABLE LVII

*Hydrogenation of Coals and Plant Materials with Sodium Formate*

4 grams substance heated with 8 grams Na-formate and 8 c.c. H<sub>2</sub>O for 3 hours to 400° in autoclave of 31 c.c. capacity.

No.	Substance.	Original coal.			Hydrogenated coal.					
		Ash.	Moist- ure.	Org. subst.	Sol. in ether.		Residue.			
					g.	% of org. subst. used.	g.	Ash.*	Organic substance.	
									g.	% of org. subst. used.
%.	%.	g.	g.			g.	g.	g.		
Bituminous coal.										
1	Semi-coke from Loh- berg gas flame coal .	7.3	3.8	3.56	0.35	9.8	3.07	0.42	2.65	74.5
2	Anthracite: Lauerweg pit, Merl seam . . . . .	5.4	0.7	3.76	0.06	1.6	3.89	0.30	3.59	95.5
3	Lean coal: Roland colly., Geit- ling seam. . . . .	3.7	0.8	3.82	0.41	10.7	3.11	0.26	2.89	74.7
4	Fat coal: Osterfeld colly., Al- bert seam. . . . .	4.3	0.8	3.80	0.35	9.2	2.86	0.25	2.61	68.7
5	Gas flame coal: Lohberg colly. near Dinslaken . . . . .	8.9	3.3	3.52	1.38	39.2	2.04	0.39	1.65	46.9
6	Fat coal(spont.comb.): Trier colly. Radbod pit No. 14 seam. . .	6.7	1.1	3.69	0.97	26.3	2.45	0.55	1.90	51.5
7	Cannel coal: Deutscher Kaiser colly. Rhein I pit, No. 5 seam . . . . .	13.8	1.0	3.41	0.96	28.2	1.38	0.62	0.76	22.3
Brown coal.										
8	Semi-coke from Saxon brown coal . . . . .	19.5	6.3	2.97	0.96	32.4	2.03	0.94	1.09	36.7
9	Saxon brown coal: Riebeck Montan Works. . . . .	12.9	9.8	3.09	1.34	43.4	0.74	0.59	0.15	4.9
10	Rosenthal coal: Preichow-Wellnitz .	10.6	11.7	3.11	1.13	36.3	0.89	0.72	0.17	5.5
11	Rhenish brown coal: Union briquettes .	4.6	16.3	3.16	1.42	45.0	0.53	0.32	0.21	6.6
12	Lignite: Bad Oybin, near Zittau . . . . .	5.1	16.7	3.13	0.84	26.8	0.60	0.28	0.32	10.2
13	Ulmic acid from Rosen- thal coal by NH <sub>3</sub> .	13.1	12.6	2.97	1.10	37.1	1.02	0.88	0.14	4.7
Peat, Wood, Lignin, Cellulose, Sugar.										
14	Peat (Oldenburg) . .	1.2	13.1	3.43	0.83	24.2	0.59	0.43	0.16	4.7
15	Wood charcoal . . .	5.3	6.0	3.55	0.21	5.9	3.27	0.44	2.83	79.7
16	Beech sawdust . . .	0.9	9.9	3.57	0.70	19.6	0.26	0.18	0.08	2.2
17	Fir sawdust . . . . .	0.3	9.6	3.60	0.70	19.5	0.26	0.17	0.09	2.5
18	Lignin (Goldschmidt)	3.3	12.6	3.36	0.75	22.3	1.67	0.48	1.19	35.4
19	Cellulose (Kahlbaum)	0.3	7.0	3.71	0.48	12.9	0.39	0.27	0.12	3.2
20	Cane sugar . . . . .	—	—	4.00	0.69	17.3	0.44†	0.37	—	—

\* The ash in the residue is not identical with the ash in the original sample, as it is partly converted into carbonate and has picked up some iron oxide from the autoclave.

† The residue is soluble in dilute hydrochloric acid except for a small amount of black carbonaceous powder.

and the coal residue on heating gave some oil. At 450°, very little oil, light reddish-brown, mobile and nearly clear, was produced; the black-brown residue did not intumescence, and gave no oil. Owing to the high temperature the bulk of the oil formed had been gasified. On opening the autoclave a large quantity of gas escaped, burning, as in other cases, with a luminous flame.

*Comparative Hydrogenation of Coal, Peat, Wood, Lignin, Cellulose and Cane Sugar*

After preliminary experiments as to the efficiency the method was applied to a series of fossil and younger plant materials; the results are tabulated in Table LVII.

All experiments were performed under identical conditions. In each case 4 grams of the material were heated together with 8 grams of sodium formate and 8 c.c. of water, to 400° for 3 hours, in the steel autoclave of 31 c.c. capacity. The reaction product was exhaustively extracted with ether. The solution, which always displayed a beautiful yellow-green fluorescence, was dried with sodium sulphate and evaporated; the quantity of residue so obtained is entered as "ether-soluble" in Table LVII. In Table LVIII the materials

TABLE LVIII

*Materials arranged according to yield of Ether-soluble Products of Hydrogenation*

(in per cent. of organic substance used)

Bituminous coal.	Brown coal.	Peat, wood, etc.
Anthracite . . . . 1.6		Charcoal . . . . 5.9
Fat coal . . . . 9.2		Cellulose . . . . 12.9
Semi-coke . . . . 9.8		Cane sugar . . . . 17.3
Lean coal . . . . 10.7		Fir wood . . . . 19.5
		Beech wood . . . . 19.6
		Lignin . . . . 22.3
		Peat . . . . 24.2
Fat coal (liable to spont. ignition) . . . . 26.3	Lignite . . . . 26.8	
Cannel coal . . . . 28.2	Semi-coke . . . . 32.4	
	Rosenthal coal . . . . 36.3	
	Ulmic acids . . . . 37.1	
Gas flame coal . . . . 39.2	Saxon carbonising coal . . . . 43.4	
	Rhenish brown coal . 45.0	

submitted to hydrogenation are arranged in the order of the percentage of ether-soluble obtained, grouped for coal, brown coal, peat, etc.

In the case of bituminous coal, the percentage of the ether-soluble products of hydrogenation under the conditions applied agrees approximately ("fat" coal and "lean" coal excepted) with the geological age, the youngest coal giving the highest yields. The yields of oil vary widely, from 1.6 per cent. in anthracite up to 39.2 per cent. in gas flame coal (ash-free, dry basis). It is noteworthy that the semi-coke of gas flame coal still gives 10 per cent. of ether-soluble products.

The figures of the two other groups come closer together. The yields from the brown coals range from 27 per cent. for lignite, to 45 per cent. for Rhenish brown coal. An examination of this group shows that the yields of ether-soluble products are not dependent upon the original bitumen content of the material. The Rhenish brown coal, which is poor in bitumen, gives higher values than the Saxon carbonising coal richer in bitumen. Hydrogenation evidently affects the non-bituminous constituents derived from lignin, and, therefore, of aromatic structure. That would also explain the resemblance in ultimate composition of the products in Table LIX to that of similarly hydrogenated primary tar phenols, which contained carbon 82.3 per cent. and hydrogen 8.9 per cent.

TABLE LIX

No. in Table LVII.	Ether soluble hydrogenation products from	C. %.	H. %.
5	Gas flame coal . . . . .	86.7	7.6
11	Rhenish brown coal . . . . .	86.0	8.6
—	Ulnic acid (at 200° from lignin) . . .	84.1	7.7
15	Beech wood . . . . .	84.0	8.8
17	Lignin (pure) . . . . .	85.0	8.2

To what extent the ether-soluble hydrogenation products contain, beside aromatic products derived from lignin, constituents of bitumen, that is, aliphatic compounds, has not yet been settled. In the case of cannel coal, a large portion of the bitumen seems to be gasified under our experimental conditions, owing to the prolonged heating to 400°; for this coal gave about 50 per cent. of gas and water as against 22 per cent. or less of volatile matter from other coals. Brown coals of various bitumen content do not exhibit such a difference.

The materials of the third group, mainly representing the plant skeleton, yield from 13 to 24 per cent. of ether-soluble hydrogenation products. Charcoal, having at the high temperature of its manufacture assumed a dense chemical structure, which is not prone to the re-formation of smaller fragments of its molecules, yields only 6 per cent. of ether-soluble. Of the other materials,

cellulose gives the lowest yield, followed by cane sugar, pine wood and beech wood arranging themselves quite properly between cellulose and lignin, according to their composition. Peat, in which ulmic constituents are already concentrated, leads on to the brown coals, beginning with lignite at 27 per cent.

In an experiment made on a somewhat larger scale in an autoclave of 116 c.c. capacity, 20 grams of powdered Union briquettes were heated with 40 grams of sodium formate and 20 c.c. of water to 400° for 3 hours.

The solid products of the reaction consisted of an oil-impregnated mixture of white salt and a dark mass. The salt was dissolved in water, and gave 8.23 grams of formate. The residue was extracted with ether, and then with water.

The ether solution was dried with sodium sulphate, and the ether evaporated. The extract yielded on distillation the following fractions :

TABLE LX

*Distillation of Ether-soluble Portion of Hydrogenated Brown Coal*

Temperature	g.	%.	Property of distillate.
100-200°	0.28	4.1	mobile.
200-250°	0.64	9.4	limpid.
250-300°	0.71	10.4	thicker.
300-350°	3.31	48.6	thin paste.
Residue	1.87	27.5	solid, dark, opaque.
	6.81	100.0	

The distillates darkened on exposure to air; the fraction from 100° to 200° turned dark yellow; the higher fractions, red with a brownish tint. On allowing the residue in the flask to "sweat" for some time over a small flame, a gentle decomposition took place and lower-boiling products continued to condense in drops; this indicates a possibility of transforming at least part of the residue into oil.

The brown coal used contained 16.3 per cent. of moisture and 4.6 per cent. of ash; 6.8 grams of ether-soluble products were obtained, representing 43 per cent. of the ash-free, dry coal substance.

A larger quantity of brown coal was then hydrogenated in the same way, but instead of extracting it with ether, 30 grams of it were directly submitted to distillation in the aluminium retort (see p. 23), the temperature being raised very gradually.

The first drops of a rather mobile tar appeared at about 300°; the later portions were of pasty consistency. The temperature was finally kept at 500° until the end of the distillation. Most of the distilled water could be

poured out from the receiver; the remainder was carefully boiled off so that tar could be weighed directly. Table LXI shows the tar yield.

TABLE LXI  
*Destructive Distillation of Hydrogenated Brown Coal*

Expt. No.	Coal from Expt. No. (Table LV).	Kind of distillation.	Product of distillation.	
			Tar % of ash-free dry coal.	Coke % of dry coal.
1	1	ordinary	27.3	—
2	2	"	26.6	—
3	3	"	23.2	48.8
4	3	"	23.0	50.3
5	3	"	26.6	—
6	4	steam	35.1	53.1
7	5	—	21.9	61.1
8	5	steam	30.0	51.3

These tar yields are very high. Some equal the yields obtainable by ether extraction, one (Expt. 6) even exceeding them by about 10 per cent. The preservative action of steam upon the tar yield (Expts. 6 and 8) is very marked. Incidentally steam counteracts the tendency to intumescence.

The tar of Expt. 1 was redistilled, yielding 1 c.c. of a rather mobile oil, 1 c.c. of a mass which congealed to ointment consistency and 1.7 grams of a thicker pasty residue of very high boiling point.

The residue was soluble in hot alcohol, with the exception of a little brown matter; on cooling, a large quantity of yellow scales separated out. The hydrogenation of diverse coals and plant products thus confirms the facts observed by various experimenters that the yield is inversely proportional to the geological age of the fuel treated. The ether-soluble reaction products are, throughout, substances of high boiling range. By distillation and partial decomposition they can be transformed into oily products, still of high boiling point. The properties of the undistilled ether-soluble products will be discussed later, in connection with the experiments of Bergius. It should be emphasised that hydrogenation of coal, by means of sodium formate under our experimental conditions, resulted in no case in a completely liquid product.

#### (d) HYDROGENATION BY MEANS OF CARBON MONOXIDE AND WATER

The following experiments were made in a steel autoclave of 118 c.c. capacity, with Rhenish brown coal (Union briquettes), as in the formate experiments. The results of the first series are given in Table LXII.

In the first experiments brown coal was heated by itself; in the second

experiment water was added to the extent of twice the weight of the coal. The yields, 4.8 per cent. and 7.6 per cent. of ether-soluble products, agree with the previous result with smaller quantities in that the presence of water favours the formation of ether-soluble matter.

In the presence of hydrogen (Expts. 3 and 4) yields were still greater, 11.1 and 13.5 per cent., and this time, again, the higher figure was obtained when water was present. Expt. 5 shows the effect of carbon monoxide upon brown coal in the absence of water, when 12.5 per cent. of ether-soluble products was obtained, approximately the same as with hydrogen. The hydrogenating effect of carbon monoxide in the absence of added water must be ascribed to the moisture in the coal, and to the water formed by decomposition.

TABLE LXII

*Comparative Hydrogenation of Rhenish Brown Coal (Union Briquettes) with Hydrogen and Carbon Monoxide.*

20 grams brown coal heated for 3 hours to 400° in iron autoclave of 118 c.c. capacity; gas pressure at room temperature.

Expt. No.	Added.		Ether-soluble reaction product.		Carbonaceous residue.				CO <sub>2</sub> formed. l.
	Gas.	H <sub>2</sub> O. c.c.	g.	% of ash-free dry coal.	g.	Ash. g.	Organic substance. g.	Solubility in pyridine. %	
1	—	—	0.75	4.8	10.25	0.17	10.08	little	1.67
2	—	40	1.20	7.6	8.87	0.79	8.08	„	1.29
3	H <sub>2</sub> at 130 atm.	—	1.75	11.1	8.51	1.03	7.48	much	2.34
4		40	2.13	13.5	8.13	0.98	7.15	45	1.20
5	CO at 140 atm.	—	1.98	12.5	9.39	1.33	8.06	much	5.38
6		40	4.7	29.7	6.31	0.94	5.37	53	7.02

The amount of ether-soluble products was very much greater, practically 30 per cent., when the coal was treated with carbon monoxide in the presence of water. We believe the superior efficiency of carbon monoxide to be due to the action of nascent hydrogen formed by the reaction between carbon monoxide and water vapour. More carbon dioxide was formed in this experiment than in any other.

Expt. 6 offers particular interest, and may be described in detail. Almost the whole of the water was, at the end of the experiment, found floating on the other products, and could be poured off. Below the water was a layer, yellow-brown in colour, and of the consistency of vaseline, with some dry, uncaked coal powder at the bottom.

These findings indicate that at 400° not only the water, but all the oily

constituents had been in the vapour phase, from which, on cooling, they were condensed above the coal.

The oily products, soluble in ether, were distilled with superheated steam in the aluminium retort. The fractions collected consisted of a brown mobile oil (15 per cent.), a yellow substance of butter consistency (40 per cent.) and a dark brown pitch-like but soft substance (12 per cent.); a dark varnish (32 per cent.) remained in the retort. On extracting 1 gram of the coal residue, insoluble in ether, with boiling pyridine, 0.53 gram was dissolved; a portion of the residue then remaining was dissolved in boiling dilute hydrochloric acid, leaving 0.37 gram of a black powder undissolved; the gas generated contained a good deal of sulphuretted hydrogen.

*Comparative Hydrogenation of Various Coals*

The comparative experiments were extended to the semi-coke from the Lohberg Colliery gas flame coal, to this coal itself and to a semi-coke from Saxon brown coal. The semi-cokes were examined because we assumed that the  $\text{CO}_2$  found in the gas after heating was a reaction product of the CO, and not of the coal, and that the  $\text{CO}_2$  was therefore a measure of the CO conversion. This assumption, it will be seen, proved erroneous in the case of the semi-coke from brown coal. The gas flame coal was selected for having given the highest yield by hydrogenation with formate.

With both semi-cokes, as Table LXIII shows, the treatment with hydrogen

TABLE LXIII

*Comparative Hydrogenation of different Coals with Hydrogen and Carbon Monoxide*

20 grams coal heated with 20 c.c.  $\text{H}_2\text{O}$  for 3 hours to  $400^\circ$  in iron autoclave. Gas compressed to 90 atmos. at room temperature.

Expt. No.	Coal.	Gas.	Ash-free dry coal used. g.	Soluble in ether.		Carbonaceous residue.		Gas blown off.		
				g.	% of ash-free dry coal.	g.	% of dry coal.	l.	CO <sub>2</sub> in gas.	
									%.	l.
1	Semi-coke from bit. coal.	CO	17.22	0.10	0.58	18.14	94.58	9.80	36.6	3.59
2		H <sub>2</sub>	17.22	0.04	0.23	18.09	94.32	7.00	4.4	0.31
3	Gas flame coal.	CO	17.57	2.32	13.20	15.20	78.55	10.26	30.4	3.12
4		H <sub>2</sub>	17.57	1.84	10.47	14.92	77.11	8.05	12.2	0.98
5	Semi-coke from brown coal.	CO	14.84	3.32	22.37	12.53	66.86	14.80	44.2	6.54
6		H <sub>2</sub>	14.84	0.22	1.48	16.15	86.18	8.16	11.4	0.93



was only slightly successful, and the yield of ether-soluble products from gas flame coal did not even come up to the tar yield in ordinary low-temperature carbonisation of the coal. The application of carbon monoxide, on the other hand, increased the quantities of ether-soluble products in all three cases. The superiority of CO was most striking in the case of brown coal semi-coke, where the amount of ether-soluble products increased fifteen times. When hydrogen was used, the quantity of carbon monoxide, which here must have been derived from the coal, was relatively high, but much smaller than that formed in the carbon monoxide experiments.

### *Influence of Pressure*

In experiments made on the hydrogenation of Rhenish brown coal with carbon monoxide and with hydrogen, an increase of pressure, from 50 to 90 atm. (in the case of the carbon monoxide, from 90 to 150 atm.), was found to exert only a moderate influence on the yield of ether-soluble products. The figures are given in Table LXIV.

TABLE LXIV

### *Influence of Pressure on Hydrogenation with Carbon Monoxide or Hydrogen*

20 grams Union briquettes and 20 c.c. water heated for 3 hours to 400° in iron autoclave of 118 c.c. capacity.

Expt. No.	Gas.	Pres. pressure.  Atm.	Ether-soluble product.		Carbonaceous residue.		Gas blown off.		
			g.	% of ash-free dry coal.	g.	% of dry coal.	l.	CO <sub>2</sub> in gas.	
								%.	l.
1	CO	140	4.7	29.7	6.3	37.63	13.5	52.0	7.02
2	"	90	3.95	25.0	7.30	43.61	10.35	41.8	4.33
3	"	50	3.51	22.2	7.47	44.62	6.27	42.4	2.66
4	H <sub>2</sub>	90	3.45	21.8	6.72	40.14	8.00	22.8	1.82
5	"	50	2.76	17.4	7.53	44.98	5.13	28.8	1.48

The further study of this problem is important, particularly for the design of apparatus required for industrial hydrogenation.

### *Influence of Temperature*

Comparative experiments on the influence of temperature were conducted at temperatures of 400°, 350°, and 450°. Details are given in Table LXV. The experiments "A" were made in an autoclave of steel; the experiments "B" in one of copper. The object was to study the influence of the material on the reaction between carbon monoxide and hydrogen, a factor to be discussed in the next section.

TABLE LXV

*Comparative Hydrogenation of Brown Coal (Union Briquettes) with Hydrogen and Carbon Monoxide at different Temperature*

20 grams brown coal and 20 c.c. water heated for 3 hours.  $H_2$  and CO compressed to 90-100 atmos. at room temperature.

Expt. No.	Temp. ° C.	Gas.	Ash-free dry coal used.  g.	Ether-soluble product.		Carbonaceous residue.			Gas blown off.		
				g.	% of ash-free dry coal.	g.	% of dry coal used.	Solubility in pyridine.	l.	CO <sub>2</sub> in gas.	
										%.	l.
A. In iron autoclave * (capacity 118 c.c.).											
1	350	H <sub>2</sub>	15.82	2.06	13.0	9.71	58.0	a little higher than at 400° and 450°.	8.0	18.3	1.47
2	350	CO	15.82	4.07	25.7	7.87	47.0	small	9.2	38.2	3.52
3	400	H <sub>2</sub>	15.82	3.45	21.8	6.72	40.1	very small	8.0	22.8	1.82
4	400	CO	15.82	3.95	25.0	7.30	43.6	small	10.4	41.8	4.33
5	450	H <sub>2</sub>	15.82	4.05	25.6	5.73	34.2	very small	7.4	23.0	1.70
6	450	CO	15.82	4.48	28.3	5.02	30.0	small	10.9	57.5	6.29
B. In copper autoclave * (capacity 130 c.c.).											
1	350	H <sub>2</sub>	15.82	3.15	19.9	8.85	52.9	about $\frac{1}{2}$	8.8	18.8	1.65
2	350	CO	15.82	3.83	24.2	8.30	49.6	very small	11.5	39.6	4.55
3	400	H <sub>2</sub>	15.82	3.30	20.9	7.25	43.3	" "	8.1	13.3	1.08
4	400	CO	15.82	3.67	23.2	7.40	44.2	" "	10.5	39.6	4.16

\* A steel autoclave completely lined with copper.

Table LXV (A) shows that the use of carbon monoxide resulted in much higher yields of ether-soluble products than the use of hydrogen at the same temperatures. A comparison of the values obtained at 400° with those of Expts. 4 and 6 of Table LXII shows that the yield with hydrogen was here exceptionally high in spite of the lower pressure (90 atm. against 130 atm.), being 21.8 per cent. against 13.5 per cent.; the yield with carbon monoxide increased, with the increase in pressure, from 25.0 to 29.7 per cent. The smaller amounts of solid coal residue found in the CO experiments corresponded to the greater yield of ether-soluble products; this residue differed from that of the experiments with hydrogen by being soluble in pyridine to the extent of one-third of the substance.

The figures of Table LXV (B) are surprising in that the yields realised at 350° were nearly as high as those obtained at 400°; in the carbon monoxide experiment a slightly higher yield was actually obtained at 350°. Here,

again, the values for carbon monoxide are higher than those for hydrogen. No experiments were made at 450° because the copper autoclave developed leakage at the higher temperature owing to the softening of the copper.

The influence of temperature was further studied in a series of experiments made with carbon monoxide at a pressure of 140 atm. between 300° and 400° (Table LXVI).

TABLE LXVI

*Hydrogenation of Brown Coal with Carbon Monoxide at different Temperatures*

20 grams Union briquettes, 40 c.c. H<sub>2</sub>O, CO under 140 atmos. pressure heated for 3 hours in iron autoclave of 118 c.c. capacity.

Expt. No.	Temp. ° C.	Ether-soluble reaction product.		Carbonaceous residue.				CO <sub>2</sub> formed.  l.
		g.	% of ash-free dry coal used.	g.	Ash. g.	Organic subst. g.	Solubility in pyridine. %.	
1	300	1.4	8.8	11.2	0.8	10.4	high	4.14
2	350	3.1	19.6	9.2	1.0	8.2	"	3.60
3	375	4.1	25.9	7.7	1.1	6.6	"	7.36
4	400	4.7	29.7	6.3	0.9	5.4	53	7.02

The yield of ether-soluble products increased considerably with the rise of temperature, from 9 per cent. at 300° to 30 per cent. at 400°.

*Influence of the Autoclave Material*

Iron is a powerful catalyst in the conversion of carbon monoxide into carbon dioxide in the water-gas reaction. When this fact is borne in mind, it may be presumed that in the hydrogenation in the autoclave at least part of the active hydrogen will come from the iron wall and another part is generated by the contact of the carbon monoxide with the coal. As far as nascent hydrogen is required by the coal, the first part would be lost. If this assumption be correct, the oil yield should be improved by substituting copper for the iron of the autoclave wall, experiments having demonstrated that by heating carbon monoxide with water for 3 hours to 400° only a little carbon dioxide was formed. Hence the parallel tests in iron and copper vessels were made (Table LXV, A and B), the results of which failed to furnish a definite confirmation of our assumption. At 350°, the copper autoclave gave a notably better yield of ether-soluble products than the iron autoclave, *i.e.*, 24.4 per cent. against 17.1 per cent.; at 400°, however, the relations were reversed, *i.e.*, 23.2 per cent. and 25 per cent.

In two further experiments made with semi-coke from brown coal, the copper autoclave proved less effective. The corresponding experiments with hydrogen gave very small quantities of ether-soluble products in both autoclaves.

To account for the failure of the hoped-for effect, it might be suggested that the carbon monoxide present was so far in excess of the proportion of the coal which could be hydrogenated that a fraction of it was quite sufficient

TABLE LXVII

*Comparative Hydrogenation of Semi-coke from Saxon Brown Coal with Carbon Monoxide and Hydrogen in Copper and Iron Autoclaves at 400°*

Expt. No.	Gas.	Initial pres- sure.	Auto- clave.	Ash- free dry coal used.  g.	Ether-soluble product.		Carbonaceous residue.		Gas blown off.		
		Atm.			g.	% of ash- free dry coal.	g.	% of dry coal.	l.	CO <sub>2</sub> in gas.	
										%.	l.
1	CO	128	Fe	14.84	3.32	22.37	12.53	66.86	14.80	44.2	6.54
2	CO	126	Cu	14.84	3.12	21.02	12.96	69.16	15.91	43.6	6.94
3	H <sub>2</sub>	90	Fe	14.84	0.22	1.48	16.15	86.18	8.16	11.4	0.93
4	H <sub>2</sub>	90	Cu	14.84	0.30	2.02	15.91	84.90	8.41	15.4	1.30

for the possible hydrogenation. In that case the expected difference between the metals would only show itself by the reduction of the quantity of carbon monoxide to the minimum required. That coal promotes the catalytic oxidation of carbon monoxide very strongly is known by the carbon monoxide experiments made in the copper autoclave, in which the proportion of carbon dioxide, after deducting that derived from the coal, as found in the hydrogen experiment, was always very considerable. For commercial work iron autoclaves would then appear to be quite suitable.

#### *Influence of Water*

Table LXVIII shows that the presence of water causes an increase in the yield of ether-soluble products. This increase was small, yet distinct, in Expts. 1 and 2 of Table LXII, made in the absence of hydrogen or carbon monoxide, and also in the hydrogen Expts. 3 and 4. The effect was very marked in the experiment with carbon monoxide, in which the hydrogenation is closely associated with the chemical interaction between carbon monoxide and water. A small series of experiments was undertaken in order to ascertain the influence of varying quantities of water on the yields of ether-soluble products in the hydrogenation with carbon monoxide. For this purpose

## CONVERSION OF COAL INTO OILS

20 grams of Rhenish brown coal and carbon monoxide were heated under pressure with 10, 20, and 40 c.c. of water for 3 hours to 400°, in a copper autoclave.

TABLE LXVIII

20 grams Union briquettes, increasing quantity of water, CO under 140 atmos. pressure, heated for 3 hours to 400° in copper autoclave of 130 c.c. capacity.

Expt. No.	Ash-free dry coal used. g.	Water used. c.c.	Ether-soluble product.		Carbonaceous residue.			Gas blown off.		
			g.	% of ash-free dry coal.	g.	% of dry coal.	Solubility in pyridine.	l.	CO <sub>2</sub> in gas.	
									%.	l.
1	15.82	10	2.20	13.9	6.92	41.3	about $\frac{1}{3}$	17.5	22.8	3.99
2	15.82	20	4.65	29.4	7.02	41.9	$\frac{1}{3}$	17.5	35.4	6.2
3	15.82	40	5.56	35.1	6.71	40.1	almost completely	11.58	44.4	5.1

With increasing proportions of water the yield of ether-soluble products was observed to improve considerably.

Hydrogenation of coal by means of carbon monoxide and water vapour becomes more complete as the pressure of the carbon monoxide, the quantity of water, and the temperature are increased. The temperature rise should probably be limited to 500°, in view of the instability of the products. Better results could certainly be anticipated if the hydrogenation were performed in an apparatus admitting of a circulation of the gas, and of a continuous removal of the volatile products. Owing probably to the liberation of nascent hydrogen, hydrogenation is, under otherwise equal conditions, more satisfactory with carbon monoxide and water than with molecular hydrogen, but less complete than with the use of an equivalent amount of sodium formate, as Table LXIX shows.

TABLE LXIX

*Ether-soluble Substance formed by Hydrogenation at 400°*

Per cent. of organic substance used.

	With carbon monoxide. %.	With sodium formate. %.
Semi-coke from bituminous coal . . . . .	0.6	10
Gas-flame coal . . . . .	13	39
Semi-coke from brown coal . . . . .	22	32
Rhenish brown coal . . . . .	35	45

As in the experiments with sodium formate, relatively small quantities of oily products are obtained under our conditions of working. The bulk of the

product is soluble in ether, but of pasty consistency at ordinary temperature. The residue of the ether extract is frequently soluble in pyridine.

(e) HYDROGENATION WITH SODIUM CARBONATE AND HYDROGEN

Subsequently to the hydrogenation experiments described, H. Schrader<sup>153</sup> observed that formate is produced when sodium carbonate solutions are heated with hydrogen under pressure. On my suggestion, A. Jaeger\* investigated whether solutions of sodium carbonate and hydrogen under pressure could be substituted for the finished formate or for  $\text{CO} + \text{H}_2\text{O}$ .

The Rhenish brown coal (Union briquettes) used in these experiments contained 1.2 per cent. of ether-soluble constituents. 25 grams of the briquettes were heated with 100 c.c. of *N*-sodium bicarbonate solution for 2 hours to 400°, in a high-pressure autoclave at various hydrogen pressures, with the results given in Table LXX.

TABLE LXX.

Expt. No.	Initial hydrogen pressure.	Ether-soluble product obtained % of ash-free dry coal.
1	20	10
2	60	19
3	100	36

As the initial hydrogen pressure was increased, the percentage of ether-soluble product increased in a marked degree, and hydrogenation became more complete. The coal residue was caked, indicating changes of the ether-soluble portion.

In order to ascertain whether the partial conversion of sodium bicarbonate into formate was really essential for hydrogenation, no bicarbonate was used in the next experiment, 25 grams of powdered brown coal and 100 c.c. of water being heated to 400° for 2 hours at a hydrogen pressure of 100 atm.; the ether-soluble diminished from 36 to 10.8 per cent. The water was then omitted; 25 grams of the powdered coal were carefully ground up with 10 grams of solid bicarbonate and heated for 2 hours to 400° at a hydrogen pressure of 90 atm.; the quantity of ether-soluble constituents then amounted to 8.4 per cent. only, instead of 36 per cent. in the presence of water. Neither the bicarbonate nor the water can therefore be dispensed with. In the last experiment, the mixture of brown coal and bicarbonate was probably not so homogeneous as if an aqueous solution had been used. Whether or not the coal remained at the high temperature of 400° in contact with liquid

\* Unpublished.

water cannot definitely be stated, but it is not impossible, since the critical temperature of the solution is higher than that of pure water.

As regards the influence of temperature, a repetition of Expt. 3, of Table LXX, at 350° instead of 400°, yielded only 20 per cent. of ether-soluble products instead of 36 per cent. A continuation of the experiment for two more hours at 350°, with a fresh charge of hydrogen, did not give more than 26 per cent., nor was a temperature of 450° more favourable; at 450° the yield was 21.6 per cent. These results agree well with the observations made by Franz Fischer and H. Schrader, who, as in other experiments described in this section, found 400° the most suitable temperature for the hydrogenation of Rhenish brown coal. It has been pointed out that the coal was found to have caked considerably in the autoclave. The action of the hydrogen would then have been more impeded as the coal surface was reduced. Some further experiments were therefore made in a shaking autoclave.<sup>154</sup> This autoclave admitted of maximum pressures of 150 atm. only, and the temperature could not, therefore, be raised to 400° in the presence of water. When the *N*-sodium bicarbonate solution was shaken with hydrogen at 60 atm., and at temperatures of 200° and 300°, some formic acid (formate) was always found to have been produced. Small quantities of formate were obtained even when starting with solid bicarbonate.

The formation of formic acid having been established, the experiments of Table LXXI were made.

TABLE LXXI

*Hydrogenation of Brown Coal with Hydrogen and Sodium Bicarbonate Solution in a shaking autoclave at 300°*

Used: 10 grams powdered brown coal, 50 c.c. *N*-NaHCO<sub>3</sub> solution, 30 atmos. hydrogen.

Expt. No.	Initial hydrogen pressure.	Duration of expt. hours.	Ether-soluble obtained % of ash-free dry coal.
1	30	2	8.4
2	60	4	12.6

These experiments demonstrate that hydrogenation takes place at 300°, and at relatively low hydrogen pressure. The hydrogenation would no doubt be much improved if shaking apparatus could be designed to work at 400° and higher hydrogen pressures.

The use of solutions of sodium bicarbonate in the presence of compressed hydrogen offers a decided advantage over that of sodium formate, or of CO + H<sub>2</sub>O, as practically nothing but hydrogen is consumed, the bicarbonate or the formate produced during the reaction acting merely as carrier

or catalyst. The use of hydrogen alone (Bergius process) without catalyst gave much poorer results (11 per cent.) instead of 36 per cent. of ether-soluble products. Since  $\text{CO} + \text{H}_2\text{O}$  by itself, as well as  $\text{H}_2 + \text{NaHCO}_3$  solution, are suitable for hydrogenation, it may be supposed that the cheaper water-gas might be substituted for hydrogen when sodium bicarbonate is applied.

It may finally be assumed that hydrogenation with compressed hydrogen without bicarbonate solution might be improved by mixing the hydrogen (or the water gas) with carbon dioxide, which together with hydrogen will form the reactive formic acid as an intermediate product. This supposition should be put to the experimental tests, and the hydrogenation experiments outlined in this section should be carried further for the purpose of ascertaining whether the bulk of coal can be really converted into oil by any of these methods.

The Bergius hydrogenation experiments, which will be further discussed below, are made with molecular hydrogen. The material (gas flame coal) is very finely ground and stirred with half its weight of middle oil from coal tar. Middle oil being a good solvent, it is quite possible that products soluble in ether and in pyridine are also formed in the Bergius treatment, but that they remain dissolved in the oil from which they might be recovered on distillation. The publications concerning the Bergius coal liquefaction do not mention a test of this kind. If the supposition is correct, his results would not prove complete liquefaction of coal any more than ours do; his liquefaction would be apparent, and of the nature of a solution process.

## (f) DESTRUCTIVE DISTILLATION OF BITUMINOUS COAL AT HIGHER HYDROGEN PRESSURES

The experiments of Franz Fischer and H. Schrader were preceded by those of Franz Fischer and Konrad Keller<sup>155</sup> towards the end of 1914. They were made in a high-pressure furnace,<sup>156</sup> suitable for temperatures of  $1000^\circ$  and pressures of 200 atm. The coal used was a fat coal (with 79 per cent. coke yield), geologically older, and hence, as the subsequent researches established, not particularly suitable for hydrogenation. These experiments, which must now be considered for various reasons as superseded, brought out two facts: First, that the tar or oil yields at high hydrogen pressure are several times greater than those obtained at ordinary pressure; and secondly, that, even at  $500^\circ$ , the amount of coke residue is inversely proportional to the hydrogen pressure, so that with rising hydrogen pressure the formation of volatile constituents, and mainly of methane, increases. This is in agreement with the experiments of Pring and Fairlie,<sup>157</sup> who showed that at high hydrogen pressure and high temperature carbon is volatilised as methane. In a prolonged experiment the coke obtained represented only 33 per cent. of the coal, and the tar and ammonia liquor, 30 per cent. The small quantities



experimented with did not permit of an accurate separation of tar and liquor; but the water was estimated as one-third of the mixture, making the tar yield about 20 per cent. as against 3 or 4 per cent. in ordinary distillation of the same coal. The experiments were arranged so as to allow the products formed by the action of hydrogen to distil at once from the hot zone of the furnace into the coldest portions and to escape further decomposition. The temperature measurements were not exact, and the results were of little more than preliminary character. Yet they establish qualitatively the possibility of a hydrogenation of coal to oils.

These experiments were not continued, as they did not seem to promise the possibility of the production of oil from coal on a large scale.

#### (g) HYDROGENATION OF COAL ACCORDING TO BERGIUS AT HIGH HYDROGEN PRESSURE

Nearly a year after the conclusion of Keller's experiments, the patents of Bergius and Billwiller were published. Although application for these had preceded Keller's work, their substance had, of course, remained unknown. An extract of these specifications is given below.

*Bergius' Brit. Pat. No. 18,232 of 1st August, 1914 (date of application in Germany, 8th August, 1914).*

"This invention relates to the treatment of coal and other solid carbonaceous material of vegetable origin formed by natural or artificial carbonisation to produce directly by chemical conversion of the carbonaceous material liquid hydrocarbons or hydrocarbons of a low melting point, and consists in subjecting the coal or the like to the action of hydrogen at pressures above 10 atmospheres, and preferably exceeding 100 atmospheres, and at an elevated temperature less than 600°. In these conditions the hydrogen reacts directly with the coal, which is transformed without destructive distillation and substantially without formation of uncondensable gases into valuable hydrocarbons which are either liquid at ordinary temperatures and pressures or which have a low melting point. The working temperature is preferably between 300° and 500° C. In place of hydrogen, gases containing free hydrogen, such as water gas, could of course also be used, or substances or mixtures which give off hydrogen, such as calcium hydride,  $\text{CaH}_2$ , the hydrogen in all cases, however, coming from a source other than the carbonaceous matter under treatment. . . .

"It is advisable to work in the presence of a solvent for the products formed during reaction, a suitable diluting medium being for instance petroleum distillates. The nitrogen of the coal is obtained in the form of ammonia in the reaction vessel.

"This hydrogenation may be combined with a carbonisation process by subjecting wood or peat or other vegetable matter to heat treatment in a hydrogen-containing atmosphere at high pressure; the hydrogen being supplied from a source different from the wood, peat, etc., under treatment, the working conditions being such that not more than very small quantities of hydrogen which are absolutely insufficient for the hydrogenation aimed at could be formed from the wood, peat, etc., under reaction.

"The products produced in the hydrogenation process consist mainly of hydrocarbons having different boiling points and which resemble chemically the mineral-oil hydrocarbons. By far the greater part of these substances is liquid at an ordinary temperature. The ash of the coal remains in the vessel as solid residues. The nitrogen of the coal escapes as ammonia with the hydrocarbons which have been distilled. The separation of the resulting condensed products can be effected in the usual manner by fractional distillation.

*Example*

"The process could be carried out for instance in the following manner: coal powder is introduced into a vessel capable of withstanding pressure, such as a steel cylinder, hydrogen at 200 atmospheres pressure is forced into it, and the whole is heated to 400° by a suitable furnace. After 15 hours, the vessel is opened, and the products generated condensed. The result is that more than half the coal is converted into a liquid substance. The unused hydrogen is recovered and used again, and the solid residues may be treated again in a similar way.

"Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

"1. A process for manufacturing liquid or easily fusible hydrocarbon compounds from coal or other solid substances produced by natural or artificial carbonisation of vegetable matter, consisting in subjecting the said substances to the action of hydrogen at a pressure of more than 10 atmospheres and at an elevated temperature not exceeding 600° C.

"2. A process as set forth in Claim 1 in which the reaction is carried out at a temperature of from 300° to 500° C. and at a pressure of more than 100 atmospheres.

"3. A process as set forth in Claims 1 and 2, in which the reaction with hydrogen is allowed to take place during the carbonising of vegetable substances.

"4. A process as set forth in Claims 1 to 3, in which the reaction is carried out in the presence of a solvent, such as petroleum distillates, for reaction products formed by the process.

"5. The process of treating coal and other products of carbonisation of vegetable matter substantially as described."

The following description of a hydrogenation experiment made in the Bergin Works at Rheinau, near Mannheim, is given by Bruylants<sup>134</sup>:— 200 grams of gas coal were mixed with 100 grams of middle oil and 200 grams of pebbles as agitating elements, in an autoclave-agitator at a hydrogen pressure of 100 atm., and slowly heated to 434°; the pressure rose to 232 atm. The temperature was kept constant at 434° for 2 hours, during which time the pressure dropped to 177 atm. After cooling, the pressure was 65 atm.

For a second experiment, the hydrogen was put under a pressure of 80 atm.; the temperature was again raised to 434° within 1 hour, during which the pressure rose to 205 atm. After maintaining the temperature at 434° for 2 hours, the pressure had dropped to 101 atm.; after cooling, the gauge indicated 68 atm. The loss of pressure in the first experiment was 35 atm., that in the second, 12 atm.; total 47 atm. The capacity of the autoclave being 5 litres, this would represent a reduction of gas volume by about 2.5 cb.m. at ordinary pressure, which may be caused by the formation of solid, liquid and gaseous compounds at the expense of the coal. The composition of the gas after the first reaction was: hydrogen 68.4 per cent., saturated gaseous hydrocarbons 13.5 per cent.; further details are not given. The composition of the gas after the second reaction was 75.2 per cent. and 11.7 per cent. respectively. On opening the autoclave, a perfectly homogeneous black tarry fluid of syrup consistency was found; it was free from solid particles, apart from the mineral constituents suspended in it.

As to the conclusion drawn, that the coal tar had been completely converted into a liquid fuel, reference should be made to the comment made at the end of the section on hydrogenation of coal by means of carbon monoxide. The fact that, in spite of the addition to the coal of 50 per cent. of thin middle oil, the product was of syrup consistency, indicates decidedly that in this experiment as in the other case the whole of the coal had by no means been transformed into a liquid fuel; but that it had been sufficiently modified, though remaining solid at the ordinary temperature, to become soluble in the oil. This interpretation might be tested by examining the residue remaining after distilling the middle oil off, when probably a pitch-like substance would be obtained. If that is so, the result of the experiment would be in accord with those obtained by hydrogenation with hydriodic acid, with sodium formate, and with carbon monoxide plus steam.

Summing up, hydrogenation of coal yields a small portion of oily products and a large portion of solid products which are soluble in certain solvents. If these solvents are added to the coal beforehand, it appears to be liquefied, though in reality it is only rendered soluble to a large extent. The fine grinding of the coal and its suspension in oil is mainly intended to facilitate charging into the autoclave by pumps. If after every charge, so as to save the supply of fresh oil, one-third were distilled off and used as

medium for suspending a new lot of coal, the total distillation residues would represent a pitch- or asphalt-like product rather than an oil. Nevertheless, the possibility of converting these products by continued hydrogenation into oily materials is not excluded. Whether this can be effected on economical lines is another question which does not come within the scope of this book. Even so, hydrogenation can at best produce high-boiling oils and only minor proportions of low-boiling ones. The size of the molecules which go to build up the coal substance must be very large in all the various types, as is evidenced by its insolubility in most solvents. For that reason, the products of the addition of hydrogen to these molecules will, on the whole, be high-boiling oils, even if a partial scission of molecules takes place.

## CHAPTER IV

### SYNTHETIC PROCESSES

THE recovery of oil from coal by dry distillation is essentially a destructive method based upon the thermal decomposition of the ulmins, and particularly of the bituminous constituents of coal. Products of low boiling range are formed only to a small extent and by a far-reaching breaking-up of the large molecules of the higher primary tar constituents. The large size of the molecules of the compounds forming coal itself explains its behaviour on distillation, *i.e.*, the fact that thermal decomposition of the bitumen and the other coal constituents yields predominantly products of high boiling points.

It is to be expected that a synthetic method, starting from very small molecules, is more likely to lead to low-boiling motor fuels than the destructive method. The simplest way of resolving coal into small molecules is to gasify it, or its carbonising residue, semi-coke or coke. It is undoubtedly advantageous first to recover the primary tar—if the coal is suitable—and then to gasify the semi-coke, as explained in Chapter III.

Carbon may be gasified by passing carbon dioxide over it at about  $900^{\circ}$  to  $1000^{\circ}$ , forming carbon monoxide according to the equation:  $C + CO_2 = 2CO - 37,320$  cals. If steam is substituted for carbon dioxide the reaction is:  $C + H_2O = CO + H_2 - 26,990$  cals. The water-gas, thus produced, is the most convenient raw material for the preparation of "Synthol."\* The fact that in generators semi-coke and coke can be almost completely converted into water-gas, with a thermal efficiency of about 80 per cent., is a promising basis for attempts at synthesising liquid combustibles from this gas.

#### (a) THE ACTION OF ELECTRIC DISCHARGES

The first experiments successful in effecting a combination of carbon monoxide with hydrogen, with the formation of liquid products, were probably those using electric discharges. Losanitsch and Jovitschitsch<sup>158</sup> submitted mixtures of CO and  $H_2$  to the silent electric discharge. The chief product obtained was formaldehyde, which was transformed into oily condensation products among which they found glycollaldehyde to predominate.

In a similar way, Berthelot<sup>159</sup> obtained a solid compound which he regarded as a carbohydrate.

Slosse<sup>160</sup> claims to have obtained from 1 vol. of carbon monoxide and 2 vols. of hydrogen, a water-soluble body of the general character of a sugar; other investigators, *e.g.*, Löb,<sup>161</sup> are not in agreement with these findings.

De Hemptinne<sup>153a</sup> replaced carbon monoxide and hydrogen by carbon monoxide and hydrocarbons, and obtained peculiar condensation products of aldehydic or ketonic character. From methane and carbon monoxide he obtained

\* The term "Synthol" has been chosen as a brief designation of the oxygenated synthetic oils produced from carbon monoxide by catalytic processes.

an aldehyde; from ethane and carbon monoxide, acetone, possibly according to the equation:  $C_2H_6 + CO = C_3H_6O$ .

Losanitsch<sup>162</sup> obtained a yellow-brown solid mass from acetylene and carbon monoxide, whilst ethylene and carbon monoxide gave a clear thick yellow-red oil. Benzene also combines with carbon monoxide under the influence of the silent electric discharge, forming a thick dark fluid.

Hultgrén<sup>163</sup> heats gaseous hydrocarbons, carbon monoxide or dioxide, in an electric high-tension arc or a spark gap to temperatures between 2000° and 4000°. The mixtures are said to condense directly, without application of pressure, to volatile oils, with heavy hydrocarbons as intermediate products. The gases are passed in a continuous stream through an electric arc, and then through a cooler, in which a portion is condensed to a very volatile liquid; 2 kilowatts are stated to be required per litre of liquid. The yield of liquid obtained varies with the material; acetylene gives 60 per cent., carbon monoxide and hydrogen give 80 per cent., carbon dioxide and hydrogen 50 per cent. of the quantity used. The unconsumed gases can be returned to the furnace. The liquid produced from acetylene boils at 85.3°, has a specific gravity of 0.723, and consists of hydrocarbons intermediate between the methane and the acetylene series. These results sound very promising, but they have so far not been confirmed by other workers.

#### (b) CATALYTIC EXPERIMENTS AT ORDINARY PRESSURE

The action of hydrogen on carbon monoxide has been the subject of many investigations. In the most noteworthy of these Sabatier<sup>164</sup> showed that, in the presence of finely-divided nickel, carbon monoxide with three times its volume of hydrogen can be converted almost completely into methane and water. At the temperature recommended, 230–250°, methane is formed rapidly, without side reactions. Above 250°, the reaction becomes more complex; carbon monoxide is then partly decomposed in the presence of nickel to carbon and carbon dioxide:  $2CO = C + CO_2$ , and this reaction becomes steadily more marked as a temperature of 250° is exceeded. The carbon dioxide formed may itself be again hydrogenated by hydrogen in contact with nickel, so that the extent of the secondary reaction:  $2CO = C + CO_2$ , must be judged not so much by the carbon dioxide formed as by the carbon deposited. At 380°, the theoretical mixture ( $CO + 3H_2 = H_2O + CH_4$ ) gives a gas of a totally different composition:  $CH_4$ , 67.9 per cent.;  $H_2$ , 21.6 per cent.;  $CO_2$ , 10.5 per cent.

At the same temperature, water-gas (equal volumes of hydrogen and carbon monoxide) in the presence of nickel gives 52.6 per cent.  $CO_2$ , 39.8 per cent.  $CH_4$ , and 7 per cent.  $H_2$ . If the carbon monoxide in the gas mixture is increased above that in water-gas, hydrogenation is further depressed, much hydrogen and carbon dioxide remaining unaltered.

Sabatier found further that carbon dioxide, like carbon monoxide, can be easily reduced to methane with nickel as catalyst:  $\text{CO}_2 + 4\text{H}_2 = 2\text{H}_2\text{O} + \text{CH}_4$ . This reaction required a somewhat higher temperature; between  $300^\circ$  and  $400^\circ$  it proceeded rapidly without appreciable side reactions. With an excess of hydrogen above the four volumes required by theory, the carbon dioxide disappears almost entirely. The gas resulting at  $300^\circ$  consists of methane, an excess of hydrogen and some carbon dioxide, and there is no deposition of carbon nor formation of carbon monoxide.

Neither the experiments of Sabatier nor corresponding technical investigations (Cedford process) indicated the formation of intermediate products, or of liquid hydrocarbons.

There are a few observations which suggest reactions in the reduction of carbon monoxide other than the formation of methane. Orloff<sup>165</sup> states that a mixture of equal volumes of hydrogen and carbon monoxide, heated to about  $95$ – $100^\circ$  in the presence of a special catalyst, yields a few per cent. of ethylene. This catalyst consisted of pieces of coke coated with nickel and palladium by impregnating them with a solution of nickel nitrate, drying and calcining them in a nickel dish over a flame; they were then impregnated with a solution of ammonium-palladium chloride, dried, and calcined. To effect reduction, they were heated in a copper tube in a current of methyl alcohol vapour, the last traces of the alcohol being expelled in a drying oven. It is not stated why hydrogen was not used for the reduction, instead of methyl alcohol, traces of which might make the results of the subsequent experiments doubtful. Two glass U-tubes were filled with the catalyst and placed in a water-bath. A current of hydrogen and carbon monoxide in equal proportions was passed through the tube, when a gas was formed of the composition: Oxygen 1.5 per cent., carbon monoxide 42.9 per cent., hydrogen 43 per cent., ethylene 6.6 per cent., nitrogen 6 per cent. An objection to these experiments is that the ethylene could not be removed with bromine water, but that after absorbing oxygen and carbon monoxide in the usual way, hydrogen and ethylene were mixed with air and burned over palladium asbestos, and the  $\text{CO}_2$  formed was absorbed by caustic potash. The objection to this course of analysis is that incomplete absorption of carbon monoxide would account for carbon dioxide in the palladium combustion. Orloff states expressly that no methane was formed at the low temperatures he employed.

In contradiction to Orloff, Breteau<sup>164</sup> claims to have found that carbon monoxide can be hydrogenated to methane with palladium as catalyst, in the cold and better at  $100^\circ$ .

Fester,<sup>166</sup> repeating Orloff's experiments, took pieces of pumice stone, impregnated them with nickel nitrate, calcined them in a nickel crucible, impregnated again with ammonium palladium chloride (1 gram of solid salt per 10 grams of pumice of pea size) and calcined again. The pumice thus prepared

was reduced by hydrogen, charged with methyl alcohol vapours, in a copper tube at  $600^{\circ}$ . After 1 hour, the tube was cooled in a current of hydrogen. Why Fester also used the quite unnecessary methyl alcohol is not intelligible; it certainly casts some doubt on the results. To repeat Orloff's experiment strictly, he would have had to use coke instead of pumice stone. The reduced pumice stone was charged into an electrically-heated glass tube, and a mixture of equal parts of hydrogen and carbon monoxide was passed over it at the rate of 2 litres per hour and at  $90-100^{\circ}$ ; before entering the tube the gas mixture was bubbled through water and dried over soda-lime. There is, unfortunately, no analysis of the gas before treatment. After leaving the catalyst tube it contained 4.7 per cent. by volume of unsaturated compounds, absorbed by bromine water. In agreement with Orloff, no methane was found. Fester states that the catalyst rapidly became ineffective, and that after a few experiments no reduction would take place.

One cannot but conclude that neither in the experiments of Orloff, nor in those of Fester, the conditions of ethylene formation were clearly recognised. It is regrettable that in both cases the catalyst was reduced with the aid of methyl alcohol; the suspicion naturally arises that the appearance of ethylene at the beginning of the experiments was due to traces of this alcohol.

Fester<sup>167</sup> recently repeated his experiments under conditions free from objections, when he did not succeed in establishing the formation of ethylene.

Medsforth<sup>168</sup> recently studied from a novel point of view the formation of methane by the hydrogenation of carbon monoxide with nickel as catalyst. He observed that the reaction is much accelerated by the addition to the nickel of promoters\*† which favour dehydration. Thoria and alumina‡ were found to be particularly active in this respect. Medsforth discusses the possibility of arresting the reaction by suitable additions to the catalyst before it reaches the methane equilibrium, and thus of obtaining interesting intermediate products. The results of several attempts made in this direction were, however, negative. Winkelmann§ has succeeded in obtaining very small quantities of formaldehyde as an intermediate product by passing water gas quickly through narrow quartz tubes, heated to  $450^{\circ}$ .

The experiments so far discussed in this section prove that liquid combustible products are not formed at ordinary pressure.

\* Kita and Mazume, *Z. angew. Chem.*, 1923, 36, 389, also proposed promoters such as alumina, magnesium oxide, magnesium phosphate, calcium phosphate and borate for the catalytic hardening of fats. The promoters to be efficient must be added before reduction of the nickel oxide, and there is an optimum quantity in each case.

† The need of securing an intimate mixture of the promoter and the catalytic metal, e.g. by common precipitation, was pointed out in a patent (D.R.-P. 307580) published in 1918, of the B.A.S.F., concerning both the reduction of carbon monoxide to methane and fat hardening.

‡ Adkins and Nissen (*J. Amer. Chem. Soc.*, 1923, 45, 809) connect the catalytic activity of  $\text{Al}(\text{OH})_3$  with the distance between the atoms, which is said to vary with the size and structure of the salt molecule from which the  $\text{Al}_2\text{O}_3$  has been prepared by calcination.

§ Unpublished.



(c) LIQUID HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN UNDER PRESSURE

In Friedländer's *Fortschritte der Teerfarbenfabrikation*, 12, 899 and 901, patents of the Badische Anilin- und Soda-Fabrik are recorded, dealing with the production of liquid hydrocarbons and their derivatives by submitting carbon monoxide and hydrogen to a contact process under pressure. The patents emphasise the fact that mainly liquid hydrocarbons are formed, and it is pointed out that in order to obtain liquid products, the hydrogen content should be reduced to, say, 1 part of hydrogen for 2 or more parts of carbon monoxide. All that is known about the process is that it does not yield the uniform products anticipated for the purposes of the chemical industry, but a very complex mixture of the most diverse bodies.

In the absence of other data in the literature, and as in the chapter on the "Synthol Process" a method will be described which works with an excess of hydrogen, whereby other products are obtained, the patents are here quoted *in extenso*.

British Patent No. 20488 of 10 Sept., 1913. Improvements in the Manufacture of Hydrocarbons and Derivatives thereof. (Corresponding German Patent No. 293787.)

"It is known that methane can be obtained from carbon monoxide, or carbon dioxide, and hydrogen at a raised temperature by means of catalytic agents (particularly nickel), and it has also been stated that by altering the conditions of the experiment, small quantities of formaldehyde and ethylene are also sometimes produced. Lipinski, in the Specification of Letters Patent No. 1325, 1913, describes the conversion of coal gas, or similar gases containing carbon monoxide and hydrogen, into methane mixture by passing the highly compressed gas, or gases, over a catalytic agent, so that the rate of reaction is increased and the conversion takes place more rapidly and efficiently.

"We have found that a new result can be obtained, and a number of organic compounds be built up, when working under pressure under suitable conditions as hereinafter explained, that is to say, we have found that easily liquefiable hydrocarbons, and oxygen compounds of hydrocarbons, can be obtained by passing a mixture, containing carbon monoxide and hydrogen in the proportion of at least two-thirds of a volume of carbon monoxide to each volume of hydrogen, over a heated catalytic agent under high pressure, that is to say, a pressure exceeding that of 5 atmospheres. The carbon monoxide and hydrogen can be passed either alone, or in admixture with other gases, over the heated catalytic agent. According to the nature of the catalytic agent employed and the conditions of working, different compounds, or mixtures, for instance, liquid hydrocarbons, either saturated, or unsaturated, and alcohols,

aldehydes, ketones and acids, are obtained. In order to obtain larger quantities of liquid compounds, it is often advantageous to employ gas mixtures in which the percentage of hydrogen contained is comparatively small, for instance, the quantity of carbon monoxide is preferably two, or three, times as much as the hydrogen reckoned by volume. As instances of catalytic agents which can be employed for the purposes of this invention, I mentioned cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc, and oxides, or other compounds of these metals, and, if desired, mixtures of two, or more, of these catalytic agents can be employed; and it is often advantageous to add a basic compound, such, for instance, as alkali hydroxide, but this invention is not limited to the use of the foregoing specific catalytic agents.

"Although the advantages of this invention can be obtained by working at any pressure above about 5 atmospheres, we prefer to employ pressure ranging say from 20 atmospheres upwards.

"The following examples will serve to illustrate how this invention may be performed, but it is not confined to these examples.

#### *Example 1*

"Impregnate pure asbestos with pure cobalt oxide, or osmium oxide, together with a little caustic soda and then, while employing a coppered iron vessel with steel jacket and working at a pressure of 100 atmospheres and a temperature of from 300° to 400° Centigrade, pass over the catalyst thus prepared a mixture containing 1 part of pure hydrogen and 2, or more, parts of pure carbon monoxide. During the reaction some carbon is deposited and some water and carbon dioxide are produced, while, in addition to methane, higher hydrocarbons, as well as oxygen derivatives of the hydrocarbons, are formed and can be at once condensed, or absorbed, in a cold receiver. Generally an aqueous solution of aldehydes and the like is obtained in addition to a light oily liquid consisting chiefly of saturated and unsaturated hydrocarbons of boiling points up to 250° Centigrade, or even higher. It is preferred to maintain the receiver under the same pressure as the reaction space and to effect the condensation by cooling. If desired, fractionated cooling can be effected, either releasing the pressure, or not.

#### *Example 2*

"Impregnate a suitable carrier (for instance, calcined magnesia, pumice stone, or diatomite) with potassium carbonate solution and then dry the mass and introduce it into a concentrated solution of zinc nitrate. Pour off the liquid, and dry and heat the contact mass and place it in a suitable vessel and, whilst employing a pressure of 120 atmospheres, and a temperature of from 360° to 420° Centigrade, pass through the vessel a gas mixture

containing 62 per cent. of carbon monoxide, 28 per cent. of hydrogen, 4 per cent. of carbon dioxide, 2 per cent. of methane and 4 per cent. of nitrogen. The products consist chiefly of higher hydrocarbons and derivatives thereof. In this case carbon is generally not deposited, or it is at most deposited to but a slight extent. The greater part of the products capable of liquefaction, or absorption, can be separated at ordinary temperature, and the remaining gas generally contains olefines, such as ethylene and propylene, and paraffins, such as methane and possibly ethane. Analysis of the products obtained shows that the oily layer consists chiefly of hydrocarbons of boiling points of from 20° to well above 200° Centigrade. For instance, one experiment yielded a mixture of which paraffins, olefines, and benzene hydrocarbons each constituted about one quarter, while the remaining quarter consisted of other hydrocarbons, both saturated and unsaturated, but these proportions will vary considerably. In addition to the said hydrocarbons, organic oxygen compounds of various kinds are contained dissolved in the hydrocarbons. The oily layer, either before, or after, special purification, has the character of the natural ethereal oils. Analysis of the aqueous layer shows a varying content of saturated and unsaturated organic compounds consisting, for instance, of alcohols, ketones (such as acetone), aldehydes (such as formaldehyde), acids (such as acetic acid and higher homologues thereof), and also other condensation products.

"When the gas mixture employed is not sufficiently pure, but contains traces of substances deleterious to the reaction, the gases may be specially purified, for instance, by passing them, before use, and at a raised temperature, through a purifier containing material similar to that employed as the catalytic agent. The gases leaving the receiver can be used over again after correcting their contents; for instance, by removing carbon dioxide and adding hydrogen, and the whole process can be carried out under continuous pressure.

#### *Claims*

"1. The manufacture of easily liquefiable hydrocarbons and oxygen compounds of hydrocarbons, by passing a mixture containing carbon monoxide and hydrogen in the proportion of at least two-thirds of a volume of carbon monoxide to each volume of hydrogen over a heated catalytic agent under high pressure, that is to say, a pressure exceeding that of 5 atmospheres.

"2. The manufacture of easily liquefiable hydrocarbons and oxygen compounds of hydrocarbons, as described in each of the foregoing examples."

German Patent No. 295202. Process of Manufacture of Hydrocarbons and their Derivatives. Addition to Patent No. 293787.

According to Patent No. 293787, hydrocarbons, particularly of liquid or liquefiable nature, and compounds derived from hydrocarbons are obtained by making oxides of carbon react at high pressure with hydrogen in the presence of catalysts.

In carrying out this process, especially in the presence of carbon monoxide in the gas mixture, it has proved advantageous to use contact materials of high thermal conductivity. By this means it is possible to avoid the possibly violent dissociation of carbon monoxide with deposition of carbon and consequent local superheating.

In the preparation of contact materials of high thermal conductivity, the catalyst deposited upon ceramic carriers may be mixed with pieces of metals such as copper and the like, granulated or in rod form; or the catalyst may be deposited upon metals of high heat-absorbing and conducting powers, or the catalytic metal may be used directly, compact in the shape of chips, wool, or wire gauze, suitably activated previously. It will be advisable at the same time to provide, by proper temperature control in the reaction chamber, for a constant temperature.

#### *Example*

Pure nickel wire gauze (*e.g.*, in the shape of rolls) suitably etched and activated by means of materials like alkali, zinc oxide, cobalt oxide, etc., is introduced into a tube capable of resisting high pressure and lined internally with copper. The tube is uniformly heated, *e.g.*, in a bath to about 350° to 400°, and a gas mixture containing 1 to 2 vols. of carbon monoxide to 1 vol. of hydrogen preheated and compressed to 100 atm., is introduced. As soon as the reaction sets in, the rate of gas feed and the heat supply and heat withdrawal are regulated; higher hydrocarbons are then formed at a uniform rate. The gas may contain small amounts of iron carbonyl.

In the special case of the preparation of acetone from acetic acid, good thermal conductors have already been used as carriers for the reacting material. This method, in an entirely different branch, did not offer any guarantee, however, that it would be possible to avoid, in the catalytic treatment of carbon monoxide-hydrogen mixtures under pressure, the diminution in the yield, sometimes occurring with deposition of carbon and the equally undesirable and occasionally dangerous, spontaneous sudden rises in temperature and pressure, by the application of the contact materials of high thermal conductivity claimed. This constitutes a surprisingly new recognition, by virtue of which an extraordinarily important effect is realised.

#### *Claim.*

The manner of carrying out the process according to Patent 293,787 by the application of contact materials of high thermal conductivity.

German Patent No. 295,203. Process for the Manufacture of Hydrocarbons and their Derivatives. Addition to Patent 293,787.

In the treatment of gas mixtures containing carbon monoxide and hydrogen under pressure with catalysts according to the process of Patents 293,787 and 295,202, the reaction is sometimes retarded when metallic catalysts are

being used, the reaction starting at a slow rate and only gradually increasing in intensity.

It has now been found that a satisfactory reaction may be secured from the beginning, when metallic catalysts are used which contain carbon chemically bound or dissolved. Suitable materials of practical utility under this heading are particularly the carbides of the metals of the iron group, as well as the metals mentioned in partly carburised form such as are obtained, *e.g.*, by treating iron with hydrocarbons or carbon monoxide with heating. Other suitable materials are, *e.g.*, cast iron, high-carbon steel, etc., in the shape of shavings, cuttings, etc., or carbides of molybdenum, tungsten, and of other suitable metals. The masses may further be activated by means of alkali and the like. For example, the reaction may be started with a gas mixture which contains, in addition to hydrogen, the same or a larger amount of carbon monoxide; this mixture is treated at 300° to 400° and at a pressure of from 50 to 100 atm.

In the synthetic preparation of ammonia from its elements, use has already been made of the carbides of the rare earths. This reaction, however, did not give any indication that it would be advantageous to use metals containing carbon as catalytic materials for this catalysis, which is of an entirely different kind.

#### *Claim.*

The special manner of carrying out the process of Patent No. 293,787 and the additional Patent 295,202 by the use as catalysts of metals containing carbon.

A patent application of F. Uhde deals with the production of liquid hydrocarbons from methane, in which he proposes to pass a mixture of methane and carbon monoxide over nickel at a temperature between 350° and 500° and to cool the products rapidly (U.5629, class 12 o). The point he emphasises is that the gases should only be left for a short time in contact with the catalyst, perforated nickel sheet coated with spongy nickel placed in a high-pressure nickel tube. He uses equal parts of carbon monoxide and methane at 400°, and does not mention any impregnation of the nickel. The light oil produced is stated to amount to 45 to 50 per cent. of the weight of methane used and to consist of the lower aliphatic hydrocarbons; unconsumed gas is to be re-used.

#### (d) ALCOHOLS AND FORMALDEHYDE FROM CARBON MONOXIDE AND HYDROGEN UNDER PRESSURE

Several other methods have recently been proposed for the reduction of carbon monoxide, by hydrogen under pressure, to formaldehyde and alcohol.

G. C. Calvert,<sup>169</sup> of the Metropolitan Laboratories, claims to have worked

out a new process for the production of alcohols, especially of methyl alcohol, by mixing water gas with gases varied according to the alcohol desired, and passing them through a special apparatus, particulars of which are not given. The alcohol yield is said to be 80 per cent. of the theoretical, at a cost much lower than that from wood distillation. Using products like coke dust, coal dust, or wood waste as raw materials, the alcohol would be cheap enough to serve as liquid fuel.

J. Lush <sup>170</sup> (Brit. Pat. 180,016) passes a mixture of carbon monoxide and hydrogen under a pressure of 10 atm. rapidly over catalysts consisting of a mixture of 4 parts of nickel, 1 part of copper and 5 parts of alumina, and claims to obtain large yields of formaldehyde or of its polymerised derivatives. The residual gas consists mainly of methane and hydrogen. The gas is preferably forced through the catalyst tube at an initial temperature of 300° to 400° under 10 atm. pressure, at a velocity such that the temperature does not drop below 160° to 180° before the gas leaves the catalyst. In order to promote rapid cooling, the compressed gas is led through a constriction and then into water to scrub out the formaldehyde. The activity of the catalyst is restored by periodically blowing steam through it, or by mixing steam with the compressed gas.

Patart <sup>171</sup> (French Pat. 540,543) makes mixtures of gaseous hydrocarbons, carbon monoxide and hydrogen react at high pressures, and at temperatures of 300° to 600° in the presence of Ni, Ag, Cu, Fe or other metals known to be catalysts for hydrogenation, in order to produce alcohols, aldehydes and acids of various kinds. In some cases he also mixes hydrocarbons with oxygen for the same purpose under similar conditions. The patent specification does not explain how the process is conducted in practice, nor what products have been obtained.

#### (e) METHYL ALCOHOL AND OILS BY DECOMPOSITION OF FORMATES

The supposition that the formation of reduction and condensation products of carbon monoxide would be facilitated by conditions favouring the intermediate production of formates has led to a number of investigations concerning the formation and decomposition of formates. A review of the literature on the subject will be found in *Abh. Kohle*, 1921, 6, 366. The decomposition of formates has been studied by K. A. Hofmann <sup>172, 173</sup> and his collaborators. More recently the formation and decomposition of calcium formate have been the subject of a detailed research.<sup>174</sup> The formation takes place at 160° to 180° when compressed carbon monoxide is heated at 10 to 50 atm. in a shaking or stirring autoclave, with milk of lime prepared from pure or commercial calcium oxide.

As regards the decomposition of calcium formate it was shown that

heating to a few hundred degrees will yield gas and in addition an aqueous distillate smelling of aldehyde, with a thin supernatant layer of a brownish oil. The residue of this dry distillation being calcium carbonate, the principle of a cyclic process seemed obvious, viz., to calcine the calcium carbonate to calcium oxide, to slake the lime and to reconvert it into formate by means of carbon monoxide. In this way the production of oil from carbon monoxide is undoubtedly possible.

The aqueous distillate of the decomposition of calcium formate has been investigated by Lieben and Paternò.<sup>175</sup> From 170 grams of calcium formate they obtained 12 c.c. of a liquid containing 5 c.c. of methyl alcohol, that is, about 3 per cent. of the weight of the formate. The oily film, of which only very little was obtained, yielded on steam distillation a light yellow oil, lighter than water and containing carbon 82.71 per cent. and hydrogen 11.6 per cent.; the substance thickened but did not solidify at  $-12^{\circ}$ , and it burned with a highly luminous flame.

In their study of the decomposition of calcium formate into liquid combustible products, Hofmann and Schumpelt<sup>172</sup> observed that it undergoes decomposition above  $380^{\circ}$  when it is mixed with dry, calcined quartz sand and heated in a current of moist carbon dioxide, the residue being calcium carbonate, grey with carbon particles. Calcium formate gave under the experimental conditions of Hofmann and Schumpelt a maximum of 4 per cent. of formaldehyde, acetone and methyl alcohol. In a subsequent paper, Hofmann and Shibsted<sup>173</sup> state that cautiously heated calcium formate gives little formaldehyde, but certainly acetone, a fair amount of methyl alcohol and much empyreumatic and carbonaceous matter. Not more than 17 per cent. of the total decomposition products, including gas and carbon, could be distilled.

Franz Fischer, Tropsch, and Schellenberg<sup>174</sup> investigated the decomposition of calcium formate in the aluminium retort, with and without steam, and with accurate temperature control. In the presence of steam the decomposition does not leave any carbonaceous residue; the resulting calcium carbonate was of a pure white colour. The temperature was maintained between  $420^{\circ}$  and  $430^{\circ}$  for a period of from 1 to 2 hours. The essential result is that the yield of liquid distillate (chiefly methyl alcohol) rose to 53 per cent. of the theoretical, a figure which has not yet been realised by other workers. Small quantities of oil are formed, of which the portion volatile in steam gave on analysis carbon 80.1 per cent., hydrogen 9.9 per cent., and oxygen 10 per cent. by difference. The portion not volatile in ordinary steam was distilled in a current of superheated steam; this oil differed from the other portion by being heavier than water, and gave on analysis carbon 73.7 per cent., hydrogen 8.7 per cent., and oxygen 17.6 per cent. The iodine number of the first oil was 55.2; that of the second, 31.4. An excess of lime in the

calcium formate had a deleterious influence on the yield of methyl alcohol. With an addition of aluminium oxide to the calcium formate, the formation of oil was diminished. Barium formate<sup>176</sup> gave even better oil yields than calcium formate, about 70 per cent. of the theoretical amount of methyl alcohol being obtained. Lithium formate proved decidedly less suitable than the calcium or barium salts.

A review of these experiments with respect to the conversion of carbon monoxide into methyl alcohol and oils, shows that this conversion can be effected via calcium or barium formate with a yield of from 60 to 70 per cent. of the theory, that of carbon monoxide into formate being quantitative. If it should really prove necessary first to prepare, and then to decompose formate, the use of the calcium salt would be preferable to that of the barium salt, although the latter gives better results, because the recovery of the oxide from the calcium carbonate is easier than from barium carbonate.

If it is intended to combine the formation and decomposition of the formate in one process, say, by the reaction of carbon monoxide and steam under pressure with calcium carbonate as contact material, the temperature would have to be raised to at least 400°, at which calcium formate is decomposed. The question then arises whether a production of formate is still possible at that temperature. From previous experiments<sup>177</sup> it is known that a little formic acid is actually formed at this temperature by the combination of carbon monoxide and water vapour under pressure, the yield being limited by the stability of the acid; in the presence of calcium carbonate some formate may therefore be produced.

#### (f) SYNTHOL FROM CARBON MONOXIDE AND WATER VAPOUR UNDER PRESSURE \*

The following experiments were made in the apparatus illustrated in Fig. 69. The apparatus, which is mounted on a tripod, consists essentially of three parts. The upper part, A, is a high-pressure cylinder made of Mannesmann steel tubing; it is filled with water and externally heated by a ring gas-burner, and supplies the steam to be added to the compressed carbon monoxide. The latter enters through a tube fixed in the cylinder cover, bubbles through the water and leaves the cylinder diluted with water vapour, through another tube which passes through the bottom of the vessel and terminates just below the cover, above the water level. The mixture of carbon monoxide and steam then enters into the contact vessel B, likewise a Mannesmann tube, 90 cm. long, 22 mm. internal diameter and 11 mm. wall thickness. An aluminium tube, 4 mm. wall thickness, fitted tightly over tube B serves to maintain an even temperature.

\* Unpublished experiments by Fischer and Tropsch.



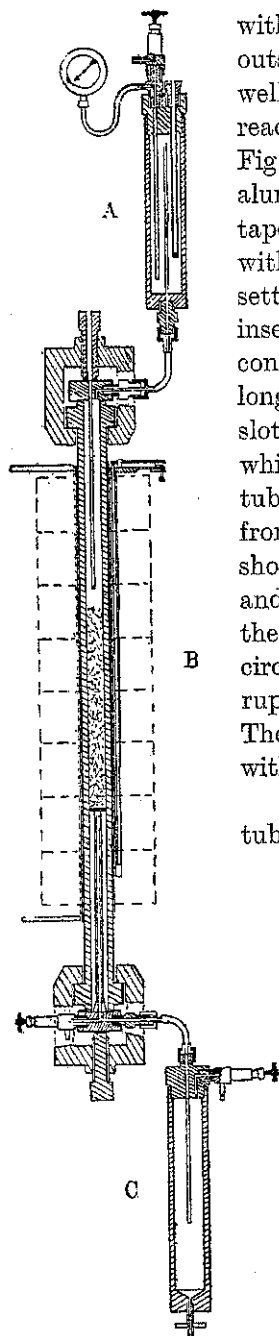


FIG. 69.

Temperature measurements were first attempted with the aid of a thermo-couple applied to the outside of the tube; later, a copper thermometer well was provided, fixed in the cover of B and reaching into the contact material, as indicated in Fig. 69. A mica insulation was wrapped round the aluminium sheath on which nichrome resistance tape was wound for the electric heating, itself lagged with asbestos. The whole tube was fixed in a setting of diatomite bricks. A thermostat was inserted in a recess in the brickwork, facing the contact tube, B. It consisted of a steel tube, 55 cm. long and 1 cm. diameter, provided with long internal slots and containing a close-fitting aluminium rod which was screwed into the lower end of the steel tube. The upper end of the steel tube, projecting from the brickwork, acted on a lever system. The short arm of the lever rested on the aluminium rod, and the lever moving with the thermal changes in the length of the rod opened or closed a battery circuit which actuated a Heraeus mercury interruptor connected with the heating current circuit. The arrangement secured temperature constancy within  $5^{\circ}$ .

Before giving further details of the contact tube, the third part of the apparatus should be

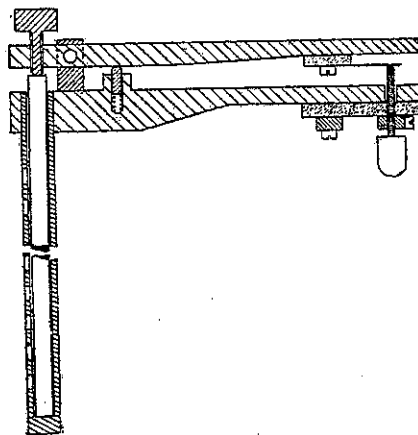


FIG. 70.

mentioned. It consisted of a Mannesmann steel tube acting as receiver for the liquid condensate from the gases which were cooled in the lower portion of B while still under pressure. The gas as freed from constituents condensable at ordinary temperature under pressure left the receiver through a reducing valve at the side and passed into a gas meter, in which the volume was determined at atmospheric pressure. The liquid condensate was withdrawn through a valve at the bottom of the receiver.

The contact tube B was tinned inside, and closed at either end by an annular copper washer held between strong steel flanges and the thick steel cover held by a clamp. The carbon monoxide entered the tube from the side through a right-angle bore so as not to be in the way of the clamp. The arrangement offered the advantage that the contact tube could easily be opened, examined and refilled without moving it. The tube was mounted vertically so as to avoid channelling in the contact material. The latter rested on a perforated plate fixed by means of clips at the lower end of the heating zone of the tube. The lower end of the tube projecting from the furnace setting was provided with a water cooler.

The carbon monoxide was stored in a steel cylinder of 40 litres capacity, from which it flowed through a copper capillary into a steel vessel charged with caustic potash to remove carbon dioxide, and then into the water vessel A.

The tubes connecting the water vessel with the contact tube B, and the latter with the receiver, were also copper capillaries. Another copper capillary penetrated through the steel cover from below into B nearly up to the perforated plate. This capillary was connected to a reducing valve in the cover. This arrangement made it possible to withdraw samples of gas at the point where it had left the catalyst; otherwise it would have been necessary when making changes in the working conditions (temperature, pressure, velocity, etc.) to wait until the whole receiver had been emptied and scavenged. The following experiments were made with this apparatus.

#### *Experiment 99*

The first contact material tried for the preparation of methyl alcohol and oil by way of calcium formate was potash lime. It was made by calcining a mixture of calcium hydroxide and potassium hydroxide in a silver dish. This mixture was used instead of calcium hydroxide, as the researches of Merz and Tibiriça<sup>178</sup> had shown that potash in the form of potash lime produces formate with special ease. It was also conceivable that potassium hydroxide acted as a carrier, transferring carbon monoxide to the calcium hydroxide. Potassium hydrate alone did not appear suitable, since on thermal decomposition potassium formate does not yield methyl alcohol as the

calcium salt is known to do. 154.5 grams of potash lime of small grain size were charged into the contact tube to form a layer 45 cm. high in the uniformly-heated middle portion of the tube. The cylinder, A, was charged with 250 c.c. of water, and the whole apparatus was put under a carbon monoxide pressure of 80 atm. The contact material was heated to 420°, the water vessel to 250°. The rate of gas discharged was kept, on an average, at 150 litres per hour; later it was reduced to 30 litres. Commercial carbon monoxide was used of the composition :—

CO <sub>2</sub>	.	.	.	5.1 per cent.	H <sub>2</sub>	.	.	.	8.5 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.3 "	CH <sub>4</sub>	.	.	.	0.3 "
O <sub>2</sub>	.	.	.	0.2 "	N <sub>2</sub>	.	.	.	3.4 "
CO	.	.	.	82.2 "					

A trace of oil was produced in the experiment of 6 hours' duration, but nearly 19 c.c. of an aqueous fluid were withdrawn from the receiver. The liquid had a faintly acid reaction and contained possibly traces of alcohol. It required 9.1 c.c. of *N*/10-NaOH for neutralisation. Traces of esters seemed to be present, for after standing for some time the colour was discharged, and a further 0.6 c.c. of *N*/10-NaOH was required. On opening the contact tube a few drops of a liquid were found condensed on the lower part; they smelled distinctly of methyl alcohol and could be lighted with a match. The contact mass had caked to a cement in which some carbon was deposited. A sample of gas taken towards the end of the experiment showed a distinct change in composition :—

CO <sub>2</sub>	.	.	.	15.8 per cent.	H <sub>2</sub>	.	.	.	18.5 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.1 "	CH <sub>4</sub>	.	.	.	0.0 "
O <sub>2</sub>	.	.	.	0.2 "	N <sub>2</sub>	.	.	.	3.1 "
CO	.	.	.	62.3 "					

At least part of the carbon monoxide had therefore reacted with steam according to the equation:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . At the end of the experiment the water vessel contained only 12 c.c. of water; the rest had been evaporated and had combined with carbon monoxide. On the whole, the result was decidedly negative\*; the occurrence of traces of alcohol was explained by subsequent experiments.

#### Experiment 103

On the supposition that the temperature of decomposition of calcium formate might be considerably above 420°, another catalyst was chosen with which the intermediate formation of a more easily decomposable formate

\* Two earlier experiments, in which pumice stone saturated with lithium carbonate, or lumps of quicklime, had served as catalyst, had likewise been failures; no alcohol was found in the water formed.

seemed likely. Temperatures above  $500^{\circ}$  could not be risked in view of the weakening of the steel tube and the accelerated deposition of carbon. The experiments of Hofmann and Shibsted<sup>173</sup> had shown that zinc formate decomposes about  $100^{\circ}$  below calcium formate. In this experiment, 73 grams of zinc oxide and 128 grams of potassium hydroxide were fused together and mixed with 68.5 grams of pumice stone crushed to pass through a sieve of 4 mm. mesh; 142.5 grams of this mixture were used as catalyst. The water vessel contained again 250 c.c. of water; the pressure of the carbon monoxide was 80 atm. as before, but the water was heated to  $200^{\circ}$  only. The contact tube was maintained at  $400^{\circ}$ , and the rate of gas at 90 litres per hour. In the earlier stages of the experiment, the escaping gases burned with a bright luminous flame. The luminosity was due to the presence of iron carbonyl, which is only formed at the commencement of an experiment; this observation was made in nearly all the experiments and will, therefore, not be mentioned again.

During a 5-hour experiment no trace of oil and only a little water was formed. The escaping gas had again undergone a change in that carbon monoxide and water reacted giving carbon dioxide and hydrogen. With respect to the desired products, the result was negative.

At the end of the experiment the water vessel still contained 180 c.c. of water; the catalyst had turned a little darker, but there was no appreciable deposition of carbon.

#### *Experiment 107*

The contact substance was copper and potassium hydroxide prepared by moistening copper turnings with 5*N*-KOH, drying and calcining on a copper sheet; 147 grams of the mass were used. The other conditions were those of Expt. 103. The result was negative.

#### *Experiment 93*

In this instance iron filings were used as a support for the catalyst, 215 grams of filings being wetted with 5*N*-KOH, dried on the water-bath and calcined in an iron crucible. The surface after cooling was grey-green and partly brown in colour. The experimental conditions differed very little from those before. There were 250 c.c. of water in the top vessel, heated to  $250^{\circ}$ ; 178.7 grams of the catalyst mass were used, heated to  $410^{\circ}$  or  $420^{\circ}$ ; the rate of gas discharge was 50 litres per hour. The escaping gas contained 30 to 40 per cent. of carbon dioxide. After 2 hours treatment 5 c.c. of a feebly acid liquid were withdrawn from the receiver, but no oil. After a further 3 hours 9 c.c. of liquid were obtained, this time including 1 c.c. of oil; the next hour yielded 5 c.c. of water and 3 c.c. of oil; the next, 5 c.c. of water and 1 c.c. of oil; and the next, 6.5 c.c. of water and 5 c.c. of oil. During

this period of water and oil production the escaping gas had the following composition :—

CO <sub>2</sub>	.	.	.	42.5 per cent.	H <sub>2</sub>	.	.	.	26.6 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.9 „	CH <sub>4</sub>	.	.	.	1.0 „
O <sub>2</sub>	.	.	.	0.4 „	N <sub>2</sub>	.	.	.	4.5 „
CO	.	.	.	24.1 „					

The gross calorific value of the oil was 8750 cals. The 27 grams of aqueous liquid gave on fractionation 0.5 c.c. boiling between 50° and 70° in which acetone was found; 1.5 c.c. between 70° and 100°, of an ester smell; the rest of the liquid was acid, and required 83.6 c.c. of *N*/10-NaOH for its neutralisation. The experiment was stopped over-night and resumed on the following day for 3½ hours; the temperature of the water vessel was somewhat lower, 215°; that of the contact tube higher, 440° on average. In 3½ hours 3 c.c. of water and 6 c.c. of oil were collected; towards the end of the experiment oil only was formed.

After completion of the experiment the water cylinder was empty, an observation reflected in the composition of the last gas sample :—

CO <sub>2</sub>	.	.	.	56.9 per cent.	H <sub>2</sub>	.	.	.	9.0 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	2.0 „	CH <sub>4</sub>	.	.	.	5.9 „
O <sub>2</sub>	.	.	.	0.2 „	N <sub>2</sub>	.	.	.	4.6 „
CO	.	.	.	21.4 „					

The small proportion of hydrogen along with the large proportion of carbon dioxide indicates that little steam entered the contact tube together with the carbon monoxide. The copious formation of CO<sub>2</sub> indicated decomposition of carbon monoxide according to the equation  $2\text{CO} = \text{CO}_2 + \text{C}$ ; this was confirmed by an examination of the contact material when as much as 37.3 grams of carbon were found deposited in it.

The diminution of the steam-carbon monoxide ratio causes a decrease of the aqueous products instead of oil. With deficiency of water vapour at high temperatures, the side reaction:  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  is substituted by the much less desirable reaction:  $2\text{CO} = \text{C} + \text{CO}_2$ , which leads to the clogging of the contact tube. The latter reaction is exothermic and is spontaneously accelerated, as becomes noticeable by the decreasing current required for maintaining the temperature.

### Experiment 111

For this experiment commercial manganese dioxide was crushed and passed through a sieve of 4 mm. mesh. The screenings were mixed with 5*N*-KOH, evaporated to dryness in a porcelain dish, and reduced by a current of hydrogen in a glass tube at 400°; 200 grams of this contact substance of manganous oxide impregnated with KOH were used. Manganous oxide was

selected in order to ascertain whether elements closely related to iron would favour the formation of oil although the presence of metallic manganese was not to be expected. The experiment was conducted much like the others and interrupted after 6 hours with the following result. The liquids which were not clear were extracted with ether giving 0.5 c.c. of oil; otherwise no oil was observed. As subsequent analysis revealed the presence of iron, the experiment does not prove the capacity of manganous oxide to induce even a small formation of oil in the presence of KOH. The water had been completely evaporated in this experiment. The temperature of the contact tube was varied occasionally between 340° and 430°, without any appreciable difference in the products. The liquid was slightly acid and it did not appear to contain methyl alcohol.

A review of these various experiments with carbon monoxide and water vapour shows that, contrary to all theoretical anticipation, considerable amounts of alcohol or oil were not formed, except when an iron support was used for the alkali. That contact with iron alone, in the absence of alkali, would not produce alcohol or oil had already been established by other experimenters.<sup>179</sup> According to the results so far obtained, the simultaneous presence of iron and alkali is required for the formation of alcohol and oil from carbon monoxide and steam. In a few further experiments nitrogen was added to the carbon monoxide in order to ascertain whether it had a disturbing influence. Large volumes of carbon monoxide are a waste product of the manufacture of calcium carbide, and still larger quantities of carbon monoxide-nitrogen mixtures are available in industry. Almost all the carbon in the coke consumed in blast furnaces reappears in the gas as carbon monoxide or dioxide. The following experiments were made, having regard to the nitrogen content of blast furnace gas, with gas containing more nitrogen than carbon monoxide.

### (g) CATALYTIC EXPERIMENTS IN THE PRESENCE OF NITROGEN

#### *Experiment 139*

Nitrogen was pressed into a steel cylinder containing carbon monoxide until the pressure rose to 113 atm. The cylinder was rolled about and turned upside down to ensure thorough mixing of the gases. The analysis of the mixed gas gave:—

CO <sub>2</sub>	.	.	.	0.0 per cent.	H <sub>2</sub>	.	.	.	1.6 per cent.
C <sub>m</sub> H <sub>m</sub>	.	.	.	0.0	CH <sub>4</sub>	.	.	.	0.0
O <sub>2</sub>	.	.	.	0.0	N <sub>2</sub>	.	.	.	56.9
CO	.	.	.	41.5					

The water vessel contained 250 c.c. of water. The contact material consisted of 230 grams of iron filings impregnated with KOH. The tem-

perature of the water vessel was kept at  $170^{\circ}$ ; that of the catalyst was varied between  $400^{\circ}$  and  $440^{\circ}$ . The rate of gas flow averaged 150 litres per hour. The gas discharged from the apparatus contained 20 to 22 per cent.  $\text{CO}_2$ . Strangely enough, no aqueous liquor was produced; when the temperature rose to  $240^{\circ}$ , oil appeared, altogether 3 c.c. in 3 hours, but no water. At the end of the experiment only 15 c.c. of water were found to have evaporated, 235 c.c. remaining in the water vessel. As there was very little steam admixed to the carbon monoxide, the conditions recall those at the end of Expt. 93, when in the absence of water, oil and no aqueous liquor was formed. On opening, the contact tube was found clogged with carbon, as in Expt. 93, the weight having increased by 24.4 grams. The experiment showed that the presence of nitrogen does not exert a disturbing influence; an appreciable formation of ammonia was not observed, and the oil yield was small. This may be partly attributed to an inadequate partial pressure of carbon monoxide. This was about 50 atm., as against the usual 80 atm. If blast furnace gas were used, it would have to be compressed to upwards of 300 atm., to ensure a carbon monoxide pressure of 80 atm., since this gas frequently does not contain more than 28 per cent. CO, as the following analysis of an average sample shows:  $\text{CO}_2$  10 per cent., CO 28 per cent.,  $\text{H}_2$  3 per cent.,  $\text{N}_2$  59 per cent. The composition of blast furnace gas may vary between these limits:—

	I	II
Carbon dioxide . . .	15 per cent.	6 per cent.
Carbon monoxide . . .	20 "	34 "
Hydrogen . . .	1 "	4 "
Nitrogen . . .	64 "	56 "

The saturation of the compressed gas with water vapour may offer difficulties. These might be obviated by mixing blast furnace gas with steam at ordinary pressure, and then passing the mixture at ordinary pressure over a contact material which will convert it into carbon dioxide and hydrogen, which can be compressed and will not require any further addition of steam. That carbon monoxide will again be formed in the apparatus was shown by the results of Expt. 144. The gas applied contained:—

$\text{CO}_2$ . . .	32.8 per cent.	$\text{H}_2$ . . .	60.5 per cent.
$\text{C}_n\text{H}_m$ . . .	0.0 "	$\text{CH}_4$ . . .	0.0 "
$\text{O}_2$ . . .	0.4 "	$\text{N}_2$ . . .	5.4 "
CO . . .	0.9 "		

Under the usual conditions the resulting gas had the composition:—

$\text{CO}_2$ . . .	33.2 per cent.	$\text{H}_2$ . . .	49.8 per cent.
$\text{C}_n\text{H}_m$ . . .	0.1 "	$\text{CH}_4$ . . .	2.4 "
$\text{O}_2$ . . .	0.2 "	$\text{N}_2$ . . .	6.2 "
CO . . .	8.1 "		

(h) CATALYTIC EXPERIMENTS WITH CARBON DIOXIDE AND HYDROGEN UNDER PRESSURE

*Experiment 144*

The composition of the gas used was as stated above. The pressure was 82 atm., temperature 420°, rate of gas flow 55 litres per hour, contact material as in Expt. 139, water vessel empty. Five to 10 c.c. of an aqueous liquid of acid reaction were made per hour; a sample on boiling yielded inflammable vapours; oil was not found. Fractionation of 37 c.c. of the alcoholic solution yielded 0.8 c.c. between 50° and 70°, in which acetone was present, and 1.7 c.c. between 70° and 100°. Later experiments indicate that the escaping gas which (as stated) contains carbon monoxide, yields oil but less water when passed a second time over the catalyst.

Having thus demonstrated that it made little difference whether carbon monoxide and steam, or carbon dioxide and hydrogen, were used, it seemed likely that commercial water gas should give similar results. Water gas is easily produced commercially and need only be freed from sulphur compounds. The following experiments were made with water gas. Carbon dioxide was at a later stage left in the gas when it was found to have actually a favourable effect in preventing deposition of carbon which the excess of hydrogen over carbon monoxide tends to cause.

(i) SYNTHOL FROM WATER GAS UNDER PRESSURE \*

In discussing these experiments with water gas, mention should first be made of Expt. 125, which was undertaken to test the statements contained in the British Patent No. 20,488/1913 (German Patent No. 293,787), of the Badische Anilin- und Soda-Fabrik (p. 206).

1. *On the need of a Metallic Hydrogen Carrier in the Contact Material.*

*Experiment 125.*

Commercial water gas was, before the compression, carefully freed of sulphur compounds, particularly  $H_2S$ , in the usual way. The contact substance was prepared by impregnating pumice stone with a concentrated solution of potassium carbonate and drying it. It was then put into a concentrated zinc nitrate solution and heated gently; the solution was poured off from the pumice, and the latter, now impregnated with alkali and zinc carbonate, was dried and heated. The catalyst was, therefore, made exactly as directed in

\* Unpublished experiments by Fischer and Tropsch.



example 2 of the specification quoted. The water gas used had the following composition :—

CO <sub>2</sub>	.	.	.	4.1 per cent.	H <sub>2</sub>	.	.	.	51.0 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.2 „	CH <sub>4</sub>	.	.	.	0.0 „
O <sub>2</sub>	.	.	.	0.2 „	N <sub>2</sub>	.	.	.	6.3 „
CO	.	.	.	38.2 „					

The contact tube was charged with 84.4 grams of the catalyst; the water gas pressure was adjusted to 90 atm.; the temperature was maintained between 400° and 420°, and the rate of gas flow at 110 litres per hour.

In this experiment not a trace of oil was obtained, and water only in minimal quantities. The water gas leaving the apparatus proved little changed by its passage over the catalyst :—

CO <sub>2</sub>	.	.	.	5.9 per cent.	H <sub>2</sub>	.	.	.	49.5 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.2 „	CH <sub>4</sub>	.	.	.	0.6 „
O <sub>2</sub>	.	.	.	0.2 „	N <sub>2</sub>	.	.	.	6.2 „
CO	.	.	.	37.4 „					

#### *Experiment 127*

The following experiment, which was made immediately after the failure of Expt. 125, demonstrates that example 2 of the specification had omitted to state some indispensable factor. The catalyst used this time consisted of 63 grams of pumice stone, which was impregnated with 30 grams of calcium acetate and 30 grams of concentrated ferric acetate solution, dried and calcined in an iron dish. Of this material, 71.5 grams were used; the pressure of the water gas, which came from the same cylinder as in Expt. 127, was slightly lower than before, viz. 85 instead of 90 atm.; temperature and rate of gas flow remained unchanged. By contrast with the last experiment, 10 c.c. of a feebly acid alcoholic liquid were obtained per hour.

The composition of the escaping gas differed considerably from that of the original water gas. It was :—

CO <sub>2</sub>	.	.	.	19.7 per cent.	H <sub>2</sub>	.	.	.	29.4 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	0.7 „	CH <sub>4</sub>	.	.	.	16.2 „
O <sub>2</sub>	.	.	.	0.8 „	N <sub>2</sub>	.	.	.	6.8 „
CO	.	.	.	26.4 „					

Why no oil was formed in Expt. 125 with potassium carbonate and reduced iron will be explained by later experiments on the influence of the bases. This experiment proves the production of an alcoholic liquor, and the changed composition of the gas further proves that the substitution of iron for zinc is essential.

## *2. Influence of the Form and Length of the Contact Material*

Although in the examples set out in the patent specification iron is not mentioned, this metal has in our method of working proved to be an essential constituent of the catalyst and is, according to our observations, far superior to cobalt and nickel.

As regards the physical condition of the metal, we found turnings preferable to fine powders; the activity of turnings sets in more slowly, but it lasts for weeks. Finely-divided iron becomes immediately active but loses its activity quickly; moreover, it always causes deposition of much carbon. The difference in behaviour of the iron turnings and powder in exothermal reactions is probably to be accounted for in the following way. The heat of reaction liberated per unit of time in 1 c.c. of contact material is proportional to the surface of the catalyst exposed within this cubic centimetre. The rise of temperature in the contact material will be inversely proportional to its heat capacity and the loss by conduction. In the finely-divided iron the heat capacity is small in comparison with the surface, and the smallness of the particles does not favour transference of heat by conduction. Conduction is further impeded by the impregnation of the iron with alkalis or alkaline earths, which are poorer conductors of heat than metallic iron. It is conceivable that finely-divided iron, properly impregnated, will immediately be fully active; but the catalyst quickly heats-up in uncontrollable fashion and accelerates the undesirable reaction:  $2\text{CO} = \text{CO}_2 + \text{C}$ , thereby clogging itself with carbon and choking the contact tube.

If the finely-divided iron particles are replaced by filings or turnings likewise impregnated, the position is at first less favourable. The active surface is small, and heat capacity and thermal conductivity are relatively very large. After starting an experiment with turnings, the catalyst gradually acquires activity. The maximum activity may only be attained after several days of continuous operation. During that period the surface of the turnings is loosened, possibly owing to an intermediate formation and decomposition of iron carbonyl. Other factors may participate in the gradual shaping of the surface of the iron turnings. It is a fact that turnings do not promote the deposition of carbon as much as finely-divided metal. In this respect, our observations are in accord with the directions given in the patent specification, that contact masses of high thermal conductivity should be applied. Expt. 263 shows the influence of the length of the contact column upon the products. In this experiment only 20 grams (instead of the usual 300 grams) of iron turnings were used; they were impregnated with 20 c.c. of  $\text{N}\cdot\text{Rb}_2\text{CO}_3$  solution, dried and heated. This small quantity of catalyst was held by a special contrivance in the middle of the contact tube; the length of the column was only 1/15 of that in the other experiments. The gas pressure,

initially 132 atm., fell to 109 atm.; the temperature of the catalyst was  $460^{\circ}$ , and the rate of gas flow 40 litres per hour. The experiment yielded 5 c.c. of an aqueous liquid per hour, containing 12 per cent. of alcohols, but only traces of oil. In 20 hours about 100 c.c. of liquor were obtained, but less than 1 c.c. of oil. The results suggest that the primary process is alcohol formation, and that the oil formation sets in at a later stage. Once the gas has left the short catalyst column, oil formation comes to an end. Oil formation thus requires for every gas velocity a minimum length of catalyst column.

### 3. Influence of Bases and their Quantity upon the Oil Yield

*Iron without Impregnation.*—If iron turnings are used alone as catalyst for water gas at 100 atm. and about  $400^{\circ}$ , methane and carbon dioxide are the chief products, whilst no oil is formed, and water only in minor quantity with no methyl alcohol.<sup>179</sup> Hence, iron without some impregnation is as ineffective, as regards alcohol and oil formation, as alkali is without iron.

*Iron with Potassium Hydroxide.*—The situation changes entirely as soon as the iron turnings are impregnated with caustic potash.\* The combination may furnish the condition for formate production. Alternatively, the alkali may act by catalytically transforming the formaldehyde, appearing as an intermediate product of the union of hydrogen and carbon monoxide, before it is reduced to the methane stage. The mechanism of the reaction will be considered in a subsequent chapter. References in the Patents of the B.A.S.F. to the impregnation of the metal as merely suitable or advantageous, but not essential, may be misleading, as according to our experience it is absolutely indispensable; without impregnation, neither alcohol nor oil is obtained, as the following experiments will demonstrate.

#### Experiment 175

300 grams of iron filings were stirred into 60 c.c. of 5*N.*-KOH in an iron dish until the mass was dry; it was then calcined. The water gas used had the composition:—

CO <sub>2</sub>	. . . . .	0.0 per cent.	H <sub>2</sub>	. . . . .	60.3 per cent.
C <sub>n</sub> H <sub>m</sub>	. . . . .	0.0 „	CH <sub>4</sub>	. . . . .	0.1 „
O <sub>2</sub>	. . . . .	0.1 „	N <sub>2</sub>	. . . . .	4.4 „
CO	. . . . .	35.1 „			

The absence of carbon dioxide in this and the further experiments in this section was secured by first passing the water gas through a steel vessel containing 2 litres of 32 per cent. caustic potash. The average temperature was  $420^{\circ}$ , the pressure 146 atm., the rate of gas flow 150 litres per hour. The average hourly yield was 9 c.c. of an aqueous liquor containing 17 per cent. of alcohols

\* Carbonate serves equally well, since the hydroxide is soon converted into carbonate.

and 3 c.c. of oil. During the 8 hours of the experiment spontaneous heating was occasionally noticed, but was quickly suppressed by cutting off the heating current; the reactions then proceeded again normally, but there was always considerable deposition of carbon in the upper portion of the catalyst. The composition of the gas leaving the contact tube was :—

CO <sub>2</sub>	.	.	.	23.8 per cent.	H <sub>2</sub>	.	.	.	41.7 per cent.
C <sub>n</sub> H <sub>m</sub>	.	.	.	3.6	CH <sub>4</sub>	.	.	.	11.5
O <sub>2</sub>	.	.	.	0.5	N <sub>2</sub>	.	.	.	5.6
CO	.	.	.	13.3					

The difference in these results from those of the experiments without impregnation or without iron (Expt. 125) is manifest both as regards alcoholic liquor and oil, and the composition of the discharged gas.

*Comparative Experiments with Different Bases.*—In a similar way a number of experiments were made, summarised in Table LXXII, in which the catalyst always consisted of 300 grams of iron turnings of the same origin and properties, which were impregnated in each case with a different base, but in equivalent quantity.

TABLE LXXII

Expt. No.	Iron filings with	Oil/hour c.c.	Water/hour c.c.	Alcohol. %.
173	LiOH	0	0.7	28
171	NaOH	0.7	4.0	24
175	KOH	3.0	8.5	17
167	RbOH	4.0	8	25
183	CsOH	3	7	19
179	Ca(OH) <sub>2</sub>	0	9	7.5
185	Sr(OH) <sub>2</sub>	0	0.9	22
181	Ba(OH) <sub>2</sub>	1.2	8.7	19

The five alkalis and the three alkaline earths are arranged in ascending order of atomic weight and therefore of basicity. It at once becomes evident that the weaker bases do not yield any oil, and that the quantity of oil, produced under otherwise equal conditions, increases with the strength of the base used for impregnation. If the weaker bases will not cause oil production, it is only to be expected that iron not impregnated at all is unable to do so. As regards oil formation, caesium hydroxide, the strongest base, seems to be an exception. This is only apparent, for on account of lack of material, impregnation was effected in this case with only 40 per cent. of the equivalent quantity. For industrial operation the provision of large amounts of caesium would be a matter of some difficulty, but rubidium should be more easily procurable. With an output of 2,000,000 tons of carnallite per annum nearly 700 tons of

rubidium chloride go into fertilisers and potassium compounds consumed by chemical industry.

*Comparative Experiments with some other Compounds.*—The experiments summarised in Table LXXII had shown that the weaker bases, though not yielding oil, would at any rate promote the formation of alcohol. Iron itself being unable to do this, it was of interest to investigate the effect of impregnating iron with basic salts and other compounds.

TABLE LXXIII

Expt. No.	Iron filings with	Oil/hour c.c.	Water/hour c.c.	Alcohol. %.
219	$K_2HPO_4$	3-0.3	11-1.6	20
221	$H_3PO_4$	0	2	8
223	$K_2SiO_3$	1.5	10	20
268	KCN	1	7	?
233	$Ba(OH)_2 + KOH$	2	5	?

The impregnation of the iron turnings was effected in the way described and all compounds were applied in equivalent proportions. The impregnation with  $K_2HPO_4$  had at first a very good effect on the formation of both oil and alcoholic liquid, but its activity diminished very much in the course of a day. An examination of the catalyst furnished the explanation; the phosphate, which to begin with had reacted strongly alkaline, had been converted into pyrophosphate, which is evidently less active.

In Expt. 221 impregnation with phosphoric acid was found to have no effect on oil formation; the want of basic properties would account for that. A little water had been formed, but it contained alcohol. It may safely be assumed that phosphoric acid had reacted with iron forming iron phosphate; it is questionable whether the phosphate was again reduced to iron in the course of the experiment. The formation of alcohol may be due to iron phosphate, and not to phosphoric acid.

Potassium silicate and potassium cyanide, being basic salts, yielded both oil and alcoholic liquor.

In Expt. 233 a mixture of bases was used, but it was found that mixed bases offered no advantages over single bases.

*Influence of the Quantity of Bases.*—Oil formation having been found to be connected with the presence of strongly basic compounds, the relation of the quantity of these compounds to the exposed surface of iron turnings was investigated. It is evident that an increase in the quantity of a weak base cannot make up for its lack of basicity; with too weak a base, no oil will be obtained, irrespective of the quantity of base used. Conversely, it was observed

that very small proportions of a sufficiently strong base promoted oil formation. With very small quantities of a base and a fixed velocity of gas, the maximum oil yield cannot be expected in view of the insufficiency of time-contact between gas and catalyst. The following experiment, and the results in the next section, give a practical illustration of the efficiency of minute quantities of a strong base.

#### *Experiment 265*

In this experiment the usual 300 grams of iron filings were impregnated with 1/20 of the quantity of  $\text{Rb}_2\text{CO}_3$  previously applied, *i.e.*, with 15 c.c. of  $N\text{-Rb}_2\text{CO}_3$  solution; the conditions were as in Expt. 263. In 14 hours, 155 c.c. of water containing 10 per cent. of alcohol and 7 c.c. of oil were obtained, or an alcohol-to-oil ratio of 2 : 1. The experiments with ample impregnation had always yielded more oil than alcohol. It must therefore be concluded that the quantity of alkali is of importance in the formation of oil at the expense of alcohol.

#### *4. Experiments with Hydrogen Carriers other than Iron*

The need of the presence of a metallic hydrogen carrier, such as iron, has been pointed out and will further be discussed in the sections on the mechanism of the reaction. It was of interest to ascertain whether iron, which necessitates a careful purification of the gas from sulphur compounds, might be replaced by other hydrogen carriers less sensitive to hydrogen sulphide, whereby sulphur compounds formed in the contact tube might be continuously reduced by the reacting gases.

*Antimony.*—After having worked the apparatus for several weeks with an iron-rubidium catalyst for the purpose of obtaining large quantities of oil for chemical examination, the contact tube was emptied, rinsed with water, and charged with a catalyst consisting of pumice-impregnated with potassium pyro-antimoniate. This compound was reduced to antimony in the course of the experiment. Antimony was chosen on the supposition that under pressure it would react with hydrogen in the water gas to form some stibine,\* which on decomposition and re-formation would act as hydrogen carrier. Expt. 247, performed under the usual conditions, seemed to confirm this supposition. Oil and alcoholic water were produced, though the oil amounted only to 1 c.c. per hour. To make sure that the appearance of the oil was due to the antimony, the contact tube was emptied and rinsed with water, and an experiment was conducted with the uncharged tube. The surprising observation was made that the iron tube, though quite empty, now gave oil and alcohol, approximately in the same quantities as before. The explanation appears to be simple. The tube had been internally tinned, in order to exclude the catalytic influence of

\* The possibility of a synthesis of stibine from hydrogen and antimony is shown by its electrolytic formation on antimony cathodes (Sand, Weeks and Worrell, *Chem. Soc. Trans.*, 1923, 103, 456).

the iron wall. In the course of the many and prolonged runs, the homogeneity of the tin-coating had suffered, iron became exposed and some rubidium salt was probably too firmly embedded in the rough surface to be washed out completely. The iron wall, impregnated in this way, was deceptive in showing activity of antimony.

The contact tube was therefore submitted to a thorough mechanical cleaning; it was then re-bored and re-tinned. In the freshly-tinned tube antimony catalysts proved quite ineffective for oil and alcohol formation. Iron with antimony (Expt. 259) gave some water and methane, which must be ascribed to the iron. Pumice stone and antimony (Expt. 257) merely yielded traces of water, and were otherwise ineffective.

*Iodine.*—A catalyst of copper turnings, superficially converted to cuprous iodide, had proved equally ineffective in a previous experiment made, when the tinning of the tube was still in good condition. The idea then was that hydrogen might momentarily form hydriodic acid, which could serve as hydrogen carrier.

In order to avoid an erroneous interpretation of further experiments owing to a damaged tin coating, a copper tube was closely fitted into the iron contact tube. It was specially tested to show that copper is completely inactive as to oil and alcohol formation, even in the presence of an alkali, in agreement with Expt. 107.

*Nickel.*—In conjunction with alkali, nickel behaved like iron and alkali, but it took longer to become active and required a higher temperature for the best yield, which even then was not so good as that with iron.

The copper sheath of the contact tube was charged with 135 grams of nickel turnings which had been evaporated to dryness with 135 c.c. of *N*-KOH. At 410°, a mean pressure of 100 atm. and a gas velocity of 40 litres per hour, practically no liquid reaction products were obtained in 50 hours. The gas remained almost unchanged, only 1.1 per cent. of methane being formed. The temperature was then raised to 450°, under otherwise unchanged conditions. After 80 hours' working, with a total consumption of 177 atm. of water gas taken from a 40-litre cylinder, which was recharged three times, 48 c.c. of aqueous and 67 c.c. of oily products were obtained. Table LXXIV gives the composition of the initial and final gases.

TABLE LXXIV

	CO <sub>2</sub> .	C <sub>n</sub> H <sub>m</sub> .	O <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	N <sub>2</sub> .
Initial gas . . .	1.2	0.0	1.7	43.0	43.7	0.0	10.4
Final gas . . .	13.0	0.0	0.0	33.5	36.9	4.2	12.4

At the end of the experiment the catalyst was found strongly attacked and disintegrated, but there was no deposition of carbon.

Table LXXV shows the results of the examination of the products of this experiment compared with an experiment made with iron under the same conditions, but at a lower temperature (410°).

TABLE LXXV

Expt. No.	Catalyst.	Alcohol per hour.	Oil per hour	Boiling range of oil.					Ultimate composition of oil fraction 80-200°.		
				Drop. °C.	80°.	100°	150°.	200°.	% C.	% H.	% O.
402	Ni	0.1	0.8	74	2	40.5	80.5	90.5	61.10	12.08	26.82
386	Fe	0.1	1.24	72	12.5	34.5	62.5	80.5	67.02	11.25	21.73

The oils obtained with nickel as catalyst contained more low-boiling constituents, particularly near 140°, than those obtained with iron, and there were considerable differences in the ultimate composition.

#### *Influence of the Composition of Water Gas \**

At this point it seems useful to discuss the influence of the composition of water gas. Nearly all experiments were conducted with a water gas in which the proportion of hydrogen was considerably higher than, and sometimes twice as high as that of carbon monoxide. This was the case whenever the water gas had been produced at a comparatively low temperature and therefore contained 10 per cent. of carbon dioxide or more. A relative diminution of the oily reaction product was never observed. After the catalyst had developed its full activity, one part of oil was produced for one or two parts of alcoholic liquor; in the previous stages the oil-water ratio was smaller. Whilst carbon dioxide had been removed in the early experiments with water gas, it was later left in the gas, without detrimental results. On the contrary, the presence of carbon dioxide as well as an excess of hydrogen over carbon monoxide seemed to exert a favourable influence in keeping down the decomposition of carbon monoxide.

In order to test the influence of gas composition upon the nature of the reaction products, three experiments were made with gases in which the carbon monoxide-hydrogen ratio varied as 1 : 2, 1 : 1, 2 : 1. Considerable differences in yield and in the nature of the product were observed, both as regards the quantities of aqueous and oily products and their proportions. The oils showed particularly striking differences in their ultimate analyses and boiling ranges.

The catalyst used consisted of 135 grams of coarse iron turnings, impregnated with 135 c.c. of *N*-KOH. The temperature was 410° in all cases. The 40-litre cylinder containing the gas mixture was connected with the contact tube at

\* Unpublished research by Fischer, Tropsch and Zerbe.



full pressure, and the pressure was allowed to drop gradually. The rate of gas discharge from the apparatus was 40 litres per hour. In Expt. 383, made with gas rich in carbon monoxide ( $2\text{CO} : 1\text{H}_2$ ), a considerable quantity of carbon was found deposited on the catalyst after 27 hours' working; the catalyst was renewed, and the experiment continued for another 30 hours with the same gas. After that time carbon deposition was considerable, and the catalyst was found disintegrated. A fresh catalyst was taken for Expt. 386 made with ordinary water gas. In this gas the turnings were little attacked and no carbon was deposited. The same catalyst was therefore used for Expt. 391, which likewise did not produce carbon deposition.

TABLE LXXVI

Expt. No.	Gas.	Gas composition.							Duration of Expt.	Gas used. Atm.	Products formed.	
		$\text{CO}_2$ %.	$\text{C}_n\text{H}_m$ %.	$\text{O}_2$ %.	$\text{CO}$ %.	$\text{H}_2$ %.	$\text{CH}_4$ %.	$\text{N}_2$ %.			aqueous c.c.	oily c.c.
391	Initial	1.8	0.0	0.6	30.7	62.0	0.3	4.6	74	112	63.8	66.4
	Final	10.7	0.0	0.0	22.1	58.9	3.1	5.2				
386	Initial	1.7	0.0	0.8	44.3	47.0	0.4	5.8	55	72	40.8	68.8
	Final	7.4	0.0	0.0	38.7	43.4	2.9	7.6				
383	Initial	7.4	0.0	0.6	55.7	29.9	0.0	6.4	69	95	15.8	122.1
	Final	28.6	1.3	0.0	41.9	16.8	2.5	8.9				

Table LXXVI summarises the composition of initial and final gases, duration of experiment, gas used in atmospheres and quantities of reaction products. The analyses indicate that the conversion was not considerable, owing to the comparatively small active surface of the catalyst, which consisted of coarse iron turnings. The reaction tended decidedly to the formation of alcohol and oil, and only small quantities of methane were formed.

TABLE LXXVII

Expt. No.	Pressure drop of gas cylinders atmos./hr.	Aqueous products c.c./atmos. total gas.	Oily products c.c./atmos. total gas.	Oily products c.c./atmos. CO.	Oily products c.c./hour.	Mean ratio aqueous : oily products.
391	1.5	0.57	0.57	1.92	1.29	1 : 1.0
386	1.3	0.57	0.96	2.16	1.24	1 : 1.7
383	1.4	0.17	1.28	2.30	2.47	1 : 7.7

As shown in Table LXXVII, the pressure drop in the steel cylinder was in all experiments approximately equal. The yield of reaction products per atmosphere of total gas varied very considerably. The oil yield was greatest with gas rich in carbon monoxide. The yield per hour was also correspondingly greater with gas richer in carbon monoxide than with gas poorer in CO. These differences become less marked when the yield is calculated per atmosphere of carbon monoxide. The water-oil ratio was 1 : 7.7 with gas rich in CO, rising to 1 : 1 with gas rich in hydrogen. The formation of small quantities of water, when using gas rich in CO, is easily explained. The water formed in the reaction is, in the presence of a large excess of CO, converted into the water gas equilibrium, as shown by the high percentage of carbon dioxide in the spent gas. With water gas rich in hydrogen, this conversion takes place to a much smaller extent and larger amounts of water are formed. In carrying out the process it will be simpler to remove the oxygen of the carbon monoxide in the form of water, which can be easily condensed, than to scrub out carbon dioxide.

TABLE LXXVIII

Expt. No.	Boiling range.						Spec. grav. of fractions.			Ultimate com- position of fraction 80-200°.		
	Drop ° C.	80°.	100°.	150°.	200°.	250°.	below 80°.	80- 200°.	>200°.	% C.	% H.	% O.
391	73	9	38	70	86.5	93.5	0.8093	0.8546	0.9647	64.78	11.05	24.17
386	72	12.5	34.5	62.5	80.5	92.5	0.7895	0.8440	0.9636	67.02	11.25	21.73
383	65	8	27	53	70	87	0.7887	0.8419	0.9588	71.10	10.73	18.17

For the examination of the products, the oil was separated from the aqueous layer, and after passing through a dry filter was submitted to fractionation in an ordinary distilling flask. The figures of Table LXXVIII were obtained with 50 c.c. of oil in each case. The oil from water gas rich in CO had the highest boiling range. The oil from gas rich in hydrogen boiled much lower, whilst that from ordinary water gas was midway between the two. The differences in boiling range are considerable. In the first case, 70 per cent. distil below 200°; in the second case, of gas rich in hydrogen, 86.5 per cent. The ultimate analyses of the fractions 80° to 200° reveal an appreciable rise in the carbon percentage with increasing percentage of the initial gas.

The specific gravity of the oil fractions was highest with the products resulting from gas rich in hydrogen.

The comparative examination of oils from water gas of different carbon monoxide percentages indicates the decided advantage of starting with a gas rich in hydrogen, for carrying out the process without deposition of carbon and

for obtaining low boiling products. Further, to secure a high rate of conversion, and when liquid products are desired, an excess of hydrogen over carbon monoxide is indispensable, and oxygen is to be removed in the form of water and not of carbon dioxide.

#### 6. *Influence of Impurities in Water Gas*

The sulphur compounds in water gas consist of hydrogen sulphide, carbon oxysulphide and carbon disulphide. The elimination of the hydrogen sulphide can be effected without difficulty by means of the ordinary gas purifying material. A preliminary treatment with slaked lime is not advisable, as the lime would also absorb carbon dioxide, which should be avoided. It is claimed to be possible to remove all sulphur compounds from the gas by passing it mixed with oxygen through activated carbon, which oxidises hydrogen sulphide to sulphur and retains the latter. The removal of carbon oxysulphide and carbon disulphide is more difficult. Whether thiophene is present in water gas is uncertain. Water gas purified with iron oxide does not blacken lead paper, but still contains other sulphur compounds easily recognised by passing the purified gas through a red-hot iron tube. Owing partly to the hydrolysing effect of water vapour in the gas, and partly to reduction by the hydrogen, hydrogen sulphide is again formed from these compounds and can, after cooling, be removed by means of iron oxide. After repeated heating and purifying, the bulk of the sulphur compounds can be transformed into hydrogen sulphide, and be removed as such.<sup>180</sup> That the removal of the sulphur from water gas cannot be carried out in a single operation is probably due to the existence, say, at 900°, of an equilibrium between carbon dioxide, hydrogen sulphide, carbon disulphide and water vapour, when most of the sulphur is present as hydrogen sulphide, but a certain amount of carbon disulphide persists. The removal of the hydrogen sulphide from the cooled gas leaves a little carbon disulphide in the gas. On reheating the gas, possibly after moistening it, the bulk of carbon disulphide is converted into hydrogen sulphide and so becomes removable. The last traces of sulphur and other impurities can be eliminated if needs be by preheating the gas with a contact material under pressure.

#### 7. *Influence of Temperature, Pressure and Gas Velocity*

By varying the temperature, leaving other conditions constant, it was ascertained that below 380° the reaction proceeds at a very slow rate. At temperatures above 450°, the tendency to deposit carbon grows. Between these limits the reaction velocity increases with rising temperature until that maximum of oil is obtained which is conditioned by its equilibrium with the other constituents in the gas. If the temperature is lower, more alcohol and less oil is produced; if higher, more oil will be found, whilst the alcohol in the aqueous liquid is diminished. Under our conditions of working, the best

results were realised at  $410^{\circ}$ . This only holds good in cases where the gas velocity is adjusted so as to leave sufficient time for the establishment of equilibrium conditions even at the lowest temperature.

As regards pressure, the ratio of oil produced to the gas discharged is proportional to it. A higher pressure accelerates by mass action the establishment of equilibrium conditions in the contact tube, and shifts the equilibrium towards the formation of the larger oil molecules. It makes their production at  $410^{\circ}$  possible to a greater extent than would a lower pressure, which would favour a tendency to decomposition of these molecules. At the maximum pressure of 150 atm. and a temperature of  $410^{\circ}$ , the formation of large molecules seems to reach a limit, for the oils obtained were almost completely volatile below  $200^{\circ}$ . It is not unlikely that at pressures of 1000 atm. and higher, the building up of large molecules might be pushed so far that solid waxes would be obtained instead of oils. It is well known that the larger the molecules of aliphatic compounds, the lower is the temperature of their thermal decomposition; the pressure must therefore be so much higher to render their formation possible. Indications of the formation of small quantities of wax-like compounds were observed (Expt. 120) when the high-boiling portions were diluted with acetone and strongly cooled, a white substance of paraffin character separating.

Thus, improved results are secured by increasing the pressure; the oil yield decreases with lower pressure, but no sharp boundary line can be drawn. Below 50 atm. the oil formation vanishes, though alcoholic liquor is still formed. Near atmospheric pressure alcohol also disappears and only methane appears as some experiments with water gas and an alkaline iron catalyst have shown.

The influence of the gas velocity is such that the maximum of oil formation is obtained at a low rate. As the velocity is raised, the oil formation decreases and more alcohol appears by comparison with the oil, as proved by the tests made with short catalyst columns (p. 223).

To sum up the influence of the three factors, pressure, temperature and velocity of gas, the most favourable temperature is about  $410^{\circ}$ , at a pressure of 150 atm.; the pressure should be as high as possible; the gas velocity should, when oil production is aimed at, be lowered until the best oil yield is reached. It is obvious that the treated gas after being freed of the liquid products may be pumped back into the cycle, over and over again,\* until it is practically spent, when its composition can be corrected by adding either hydrogen or carbon monoxide. Alternatively, it may, without the aid of a pump, be passed under its own pressure over a fresh catalyst until it is spent. Experiments with a continuous circulation apparatus are described in the next section.

To discuss all factors which were found to affect the yields and the safety

\* Carbon dioxide might be continually removed and olefines extracted with concentrated  $\text{H}_2\text{SO}_4$ . The oil formed has the general formula  $\text{C}_n\text{H}_{2n}$ .

of working, in the course of several years of investigations, is beyond the scope of this book, which is intended merely to outline the essential conditions for the production of oil from water gas.

#### 8. *Determination of Yields in the Circulation Apparatus*

In the preceding experiments water gas was only once passed through the contact tube and thus badly utilised, since only a certain quantity of oil and alcohol could be formed in equilibrium with unchanged water gas, carbon dioxide, steam, and methane. It was to be expected that the gas might be re-used after the removal of the liquid reaction products, oil, alcohol and water. For this purpose, 6 cb.m. of the discharged gas were collected and compressed again to 150 atm. in a cylinder of 40-litre capacity. This gas was then fed into the contact tube under the usual conditions and yielded some oil, alcohol and water, but, in keeping with the changed composition, less than the original water gas.

*Description of the Apparatus for Continuous Circulation.*—In order to arrive at some estimate of possible yields, the apparatus illustrated in Fig. 71 was constructed.

The contact tube of the apparatus consists of a Mannesmann tube, 110 mm. external diameter and 10 mm. wall thickness, closed by a cap at the lower end. The compressed gas enters through the cap and rises through an annular space, of 17 mm. clearance, between the outer steel tube and a copper tube reaching nearly to the top. The upper portion of the copper tube is charged with the catalyst, resting on a perforated disc. The upper end of the steel tube is closed and drilled to admit a pocket for the thermo-couple with its junction close to the catalyst.

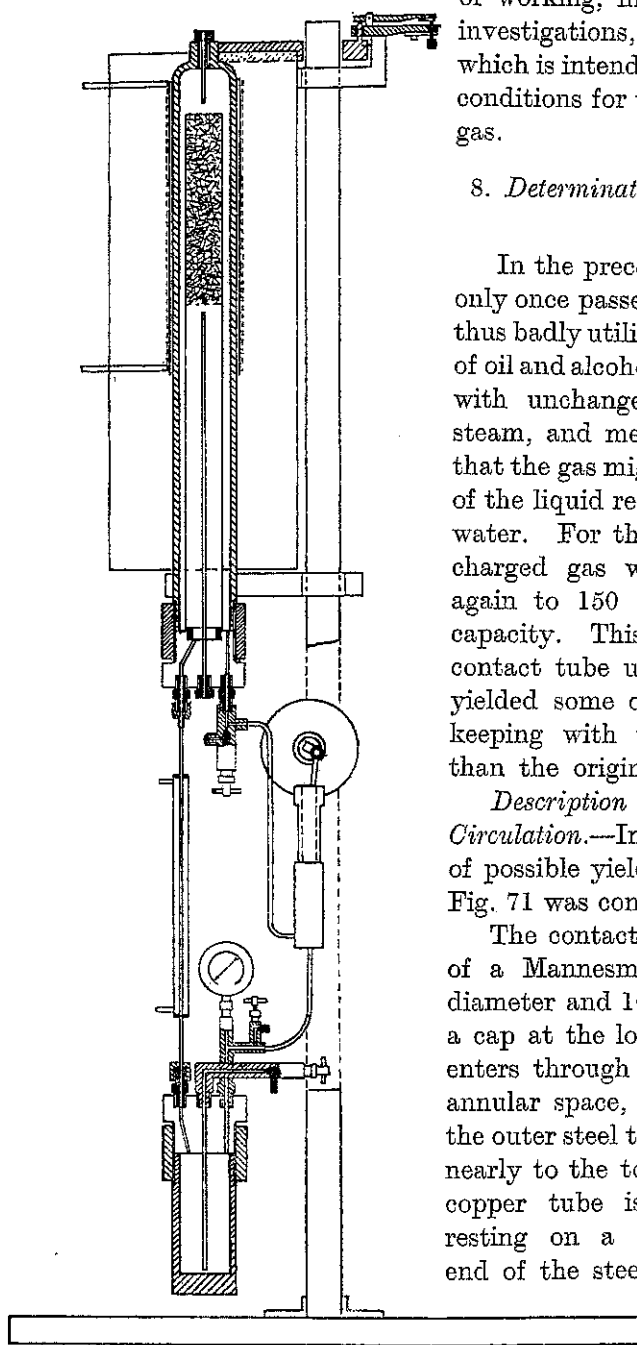


FIG. 71.

After rising, the gas flows down the copper tube, leaves through a bore in the cap and flows through a high-pressure condenser into the receiver, where the liquid products are deposited. From the receiver the gas is withdrawn by the circulation pump and returned to the contact tube.

Only the upper portion of the steel tube is electrically heated; the lower half together with the copper tube serves as heat exchanger. The rising gas is preheated to the reaction temperature in the annular space before it reaches the catalyst on its downward path. After leaving the catalyst, it heats the lower part of the tube and the ascending gas outside it. An efficient temperature equalisation and control was thereby secured. The catalyst consisted of fairly coarse iron turnings, about 1 sq. mm. cross-section, impregnated with potassium carbonate and loosely packed in the copper tube to admit of a rapid passage of gas. The circulation pump was mostly set for moving 150 c.c. of compressed gas per minute. Without circulation the gas was clear of the catalyst after 20 minutes; with the aid of the pump it could be returned five times per hour. In addition, it was possible to keep one charge of the contact tube in circulation by itself. The steel vessel had 3 litres free space; the receiver could accommodate 1 litre of liquid. The pressure fluctuations of the alternating currents used for heating made an automatic temperature control necessary. This was simply effected by allowing the expansion of the steel tube to open or close, through lever mechanism, a low-tension circuit, which actuated a Heraeus mercury interruptor, which in its turn controlled the heating current. For this purpose the lower end of the steel tube was firmly clamped in a standard; a clip round the upper end of the tube was free to move up and down on the standard. By this very crude method, the temperature was easily kept constant within  $5^{\circ}$ , though fluctuations in the current supply were considerable. The steel tube was wound with nichrome wire, which could easily be detached, and required 14 amperes for heating. It was lagged with diatomite bricks 5 cm. thick.

#### *Experiment 316*

The catalyst for this apparatus was prepared by evaporating 740 grams of coarse iron turnings with 740 c.c. of *N*-KOH, and calcining in an iron crucible. The catalyst was charged into the upper half of the copper tube. The temperature was  $410^{\circ}$ ; the pressure 102 atm. The gas leaving the apparatus \* had the composition:—

$\text{CO}_2$ . . . . .	22.8 per cent.	$\text{H}_2$ . . . . .	55.0 per cent.
$\text{C}_n\text{H}_m$ . . . . .	1.0 "	$\text{CH}_4$ . . . . .	0.8 "
$\text{O}_2$ . . . . .	0.4 "	$\text{N}_2$ . . . . .	6.6 "
$\text{CO}$ . . . . .	19.3 "		

The apparatus having been heated to constant temperature, the connection with the steel cylinder and the outlet valve was closed. The pump was then

\* The composition of the gas from the cylinder is here immaterial.

started, and the gas circulated through the catalyst.\* The pressure fell in 4 hours from 102 to 42 atm., at a rate shown in Table LXXIX.

TABLE LXXIX

Time minutes.	Temperature.	Pressure Atm.
start.	410°	102
70	410	75
100	410	68
160	410	56
180	410	52
240	410	42

As the pressure decreased, the formation of alcohol and oil diminished, but it continued right to the end. The final gas had the composition :—

CO <sub>2</sub> . . . .	32.1 per cent.	H <sub>2</sub> . . . .	10.3 per cent.
C <sub>n</sub> H <sub>m</sub> . . . .	1.1 „	CH <sub>4</sub> . . . .	19.8 „
O <sub>2</sub> . . . .	0.5 „	N <sub>2</sub> . . . .	11.8 „
CO . . . .	19.4 „		

*Thermal Balance.*—In order to ascertain the portion of heat units supplied with the gas, those present at the end of the experiment in the form of oil and alcohol, and those lost by exothermal reactions, the following calculation was made : Initial gas pressure 102 atm. Volume of apparatus † 2.8 litres = 286 litres at atmospheric pressure, or 268 litres at N.T.P. Heating value of the gas (calc.) 2480 cal. per cb.m. Heat used therefore = 665 cal.

Total calorific value of 20 c.c. of oil and 9.3 c.c. of alcohol = 192 cal. (Total yield : 20 c.c. of oil and 62 c.c. of liquor containing 15 per cent. of alcohol.)

Final pressure 42 atm. Volume of apparatus 2.8 litres = 118 litres at atmospheric pressure, or 111 litres at N.T.P. Calorific value (calc.) 3900 cal. per cb.m. Heat found therefore = 433 cal.

The output represents  $192 + 433 = 625$  cal., about 40 cal. less than the input, a loss of 6 per cent.‡ The oil and alcohol contained  $\frac{192 \times 100}{665} = 29$  per cent. Expt. 316 demonstrates that it is possible to obtain at least 29 per cent. of the calorific value of the water gas in the form of oil and alcohol. Considering that alcohol and oil production was still proceeding at the end

\* The condensable products, oil, alcohol and water, were collected in the receiver.

† The volume was determined with the contact tube hot, by letting off gas, until the pressure had been reduced by 10 atm., and measuring its volume.

‡ A loss of this kind occurs, for instance, in the formation of methane according to :  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 49,000$  cal. The heat value of 4 cb.m. of  $(\text{CO} + 3\text{H}_2)$  is about 12,000 cal.; that of the resulting  $\text{CH}_4$ , only 9500 cal.

of the experiment, though the pressure had dropped to 42 atm., it may be safely concluded that even higher calorific yields in the form of liquid fuels are possible. The results would certainly have been better by working at constant, instead of diminishing, pressure.

Experiments in this direction will be made with eight contact tubes connected in series; condensers for the reaction product will be inserted after every two tubes.

On calculating the results of Expt. 316 for the quantity of water gas, disregarding difference between calorific values of initial and final gas, it is found that 268 litres of water gas gave about 30 c.c. of liquid fuel; that would be approximately 112 c.c. = 100 grams per cb.m. From 10 cb.m., or 7 kg., of water gas about 1 kg. of liquid fuel is even now obtainable with a thermal efficiency of 29 per cent. On the basis of the latter, one may, under favourable conditions, reckon upon 3 kg. of liquid fuel from 10 cb.m. of water gas, provided no combustible gas is left. The spent gas from Expt. 316 had a calorific value of 3900 cal. in spite of the high carbon dioxide content of 32.1 per cent. If carbon dioxide were washed out, a gas of about 6000 cal. would remain, with a consequent rise in nitrogen from 12 per cent. to 18 per cent.

#### (k) CARBON DIOXIDE AND HYDROGEN IN THE CIRCULATION APPARATUS

##### *Experiment 329*

It has been shown (Expt. 144, p. 221) that from carbon dioxide and hydrogen in the ratio 1 : 2 no oil but much water and a little alcohol were obtained. It was also observed that the spent gas contained 8.1 per cent. carbon monoxide formed by a reduction of carbon dioxide, though steam was present. It was then suggested that the spent gas would yield oil on passing it, after cooling, a second time through the catalyst. This was tested in the circulation apparatus, but the excess of hydrogen was made larger than in Expt. 144, so as to reduce the carbon dioxide to the  $\text{CH}_4$  stage.

The apparatus was charged from a gas cylinder at a pressure of 135 atm., and the connection with the cylinder was closed. The composition of the gas was:—

$\text{CO}_2$ . . . . .	24.0 per cent.	$\text{H}_2$ . . . . .	73.6 per cent.
$\text{C}_m\text{H}_m$ . . . . .	0.0 „	$\text{CH}_4$ . . . . .	0.0 „
$\text{O}_2$ . . . . .	0.1 „	$\text{N}_2$ . . . . .	2.3 „
$\text{CO}$ . . . . .	0.0 „		

The catalyst consisted of 470 grams of coarse iron turnings impregnated with  $\text{N-KOH}$ , as in Expt. 316. The pressure rose while the apparatus was heated to  $410^\circ$ ; circulation was then started at a rate at which the gas charge passed 5 times per hour through the catalyst. The pressure and composition of the



gas and the yield of oil and water at progressive stages are specified in Table LXXX; the water contained 5 per cent. of alcohol.

This table shows that the brisk water formation diminishes gradually; methane appeared almost suddenly after 5 hours, and heavy hydrocarbons

TABLE LXXX

Time. minutes.	Temp.	Pressure Atm.	CO <sub>2</sub> %.	C <sub>2</sub> H <sub>4</sub> %.	CO %.	H <sub>2</sub> %.	CH <sub>4</sub> %.	N <sub>2</sub> %.	Water c.c.	Oil c.c.
start	410°	115	24.0	0.0	0.0	73.6	0.0	2.3	—	—
30	410	105	14.4	0.0	11.4	69.6	0.0	4.6	8.5	—
100	410	89	8.7	0.0	19.3	66.6	0.0	5.2	27	—
215	410	28	13.4	0.0	11.1	51.7	15.7	7.9	49	1
275	410	14	11.3	11.7	11.9	33.7	25.3	11.9	13.5	4
365	410	7	8.5	15.2	6.3	20.7	35.4	13.9	7.5	2.5

1 hour later. The first oil was observed simultaneously with methane. It is interesting to note that oil formation had not ceased when the pressure had gone down to 7 atm., at which the experiment was stopped. The expectation that oil would be obtained from carbon dioxide and water is confirmed by the experiment. Repeated passage \* through the catalyst and condenser was required before the composition of the gas mixture had become amenable to oil formation, which seems to be conditioned by the presence of carbon monoxide. This appeared soon after starting, and temporarily rose to 19.3 per cent. Certain irregularities in the table disappear if the percentages are multiplied by the total pressures and divided by 100. The partial gas pressures of the graphs of Fig. 72 were obtained in this way. It is then seen that the pressures of hydrogen and carbon dioxide were continuously falling and do not show maxima and minima as in Table LXXX. The rise and fall of the carbon monoxide, methane and unsaturated hydrocarbons are well brought out. "Methane" probably includes some of its homologues; its decrease may be due to the formation of oil and alcohol, or to its conversion into homologues with loss of hydrogen.

Somewhat surprising is the occurrence of carbon monoxide when carbon dioxide is on the decrease and much water is formed. One would expect that carbon monoxide at 410° would react with steam to give carbon dioxide and hydrogen. Oil formation at such low pressures as 14 and 7 atm. is another new fact not observed in the previous experiments, which indicates that certain gas mixtures yield synthol at very low pressures. Heavy hydrocarbons (absorbed by fuming H<sub>2</sub>SO<sub>4</sub>) appear together with "methane." They amount to not less than 15 per cent. of the final gas, a higher percentage than that of carbon monoxide and carbon dioxide in the same gas sample.

\* The gas was pumped 5 times per hour over the catalyst.

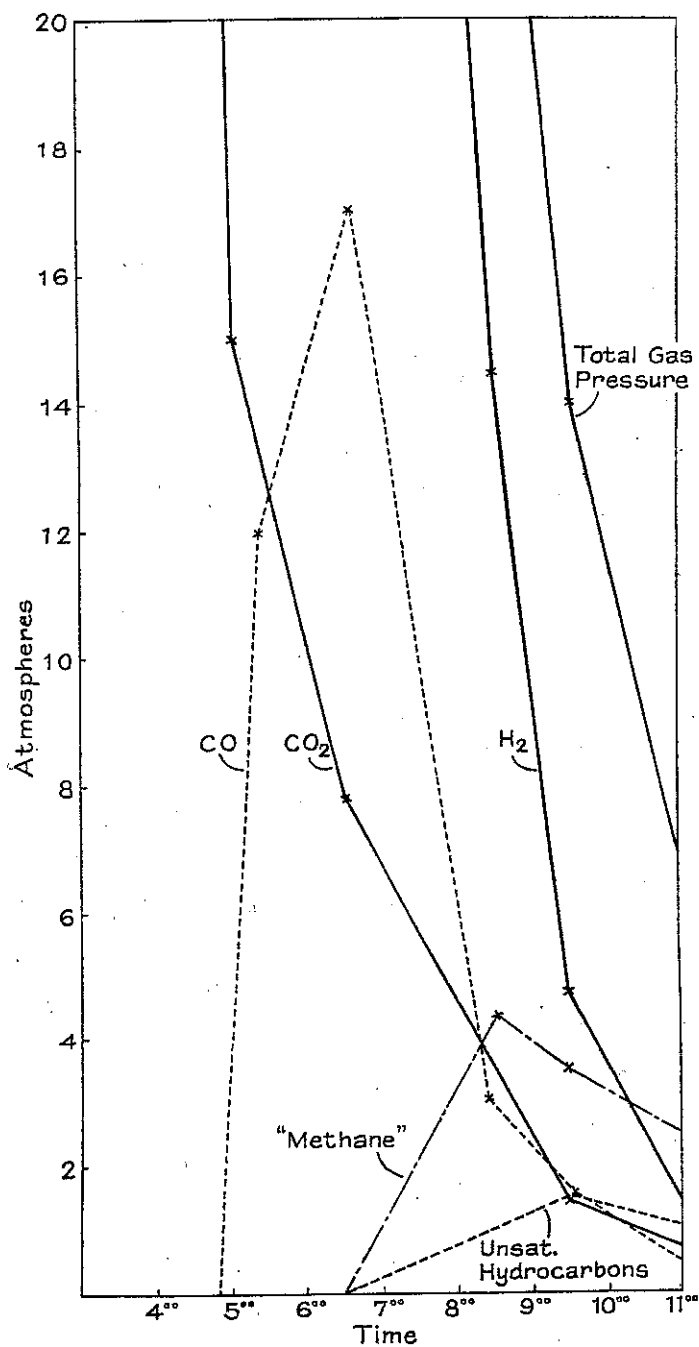


FIG. 72.

Probably the primarily-formed alcohols, found under other conditions in the water, were in this case converted with loss of water into olefines. If, for example, ethyl and propyl alcohol were converted into ethylene and propylene, the liquor would become poorer in alcohols and the gas richer in olefines. It was further observed that the high olefine content of the gas still in the apparatus decreased during cooling overnight. The olefines in the contact tube were probably converted into methane hydrocarbons by hydrogen, a reaction favoured by lower temperatures. It was indeed found that the decrease in olefines was accompanied by an increase in paraffin hydrocarbons.

The occurrence of gaseous olefines, due to the dehydration of water-soluble alcohols, has a parallel in the composition of the oil. Whilst in all previous experiments with a small excess of hydrogen the oil obtained was almost completely soluble in concentrated sulphuric acid, the oil from this experiment contained 40 per cent. of hydrocarbons of pronounced petroleum smell, insoluble in concentrated sulphuric acid. The formation of these hydrocarbons, analogous to the synthin experiments to be described later, indicates that alcohols are converted by longer treatment into hydrocarbons with the liberation of water. According to our more recent observations the formation of olefines is favoured by the presence of carbon monoxide, which reacts with liberated water yielding  $\text{CO}_2 + \text{H}_2$ , stimulating progressive dehydration.

#### (b) CARBON DIOXIDE AND METHANE IN THE CIRCULATION APPARATUS

##### *Experiment 343*

A mixture of 1 part of  $\text{CO}_2$  and 3 parts of  $\text{CH}_4$  was kept circulated over the catalyst of Expt. 229 and under otherwise equal conditions. Only traces of water, and neither alcohol nor oil, were produced. As the failure of any reaction between carbon dioxide and methane might have been due to the exhaustion of the catalyst, its activity was checked by withdrawing the gas mixture, and charging the apparatus with water gas at 120 atm. (Expt. 345). At once, ample quantities of water, alcohol and oil were obtained, proving the catalyst to be undoubtedly still in good condition.

##### *Experiment 347*

The water gas was blown off and the apparatus recharged with a 1:3 mixture of carbon dioxide and methane at a total gas pressure of 88 atm. After  $2\frac{1}{2}$  hours' working, the pressure was still exactly 88 atm.; neither water nor oil had been formed, proving definitely that under the experimental conditions employed carbon dioxide and methane do not react.

*(m)* CARBON MONOXIDE AND METHANE IN THE CIRCULATION APPARATUS*Experiment 388*

Since the decomposition of carbon monoxide into carbon dioxide and carbon is exothermic, carbon monoxide might be thought more likely to react with methane through nascent carbon. In the experiment a mixture of 1 part of carbon monoxide and 2 parts of methane was studied in the circulation apparatus. A freshly prepared catalyst of iron turnings and caustic potash was first tested with water gas. As soon as oil formation had set in, the water gas was blown off and replaced by the carbon monoxide-methane mixture. The temperature was as usual  $410^{\circ}$ ; the pressure 90 atm. The pressure was found unaltered after 3 hours; neither water nor oil was found. The experiment was continued for  $5\frac{1}{2}$  hours on the following day, again without yielding any oil or water. It is therefore certain that methane does not react with carbon monoxide. During  $5\frac{1}{2}$  hours the pressure dropped by 2 atm. The gas analysis showed that some carbon monoxide was decomposed, which according to the reaction  $2\text{CO} = \text{CO}_2 + \text{C}$  would lead to a pressure reduction. Summing up Expts. 343, 347, and 388, we find that methane cannot be converted into liquid compounds by either carbon monoxide or carbon dioxide. As a practical conclusion, in water gas experiments, methane formation should be limited when liquid products are aimed at, since methane, once formed, no longer takes part in the synthol reaction.

*(n)* EXAMINATION OF PRODUCTS OF REACTION <sup>181</sup>

The object of the researches of this section, dealing with the utilisation of carbon monoxide and water gas, was the production of liquid low-boiling motor fuels regardless of their chemical uniformity.

Contrary to the endeavours of the B.A.S.F. to prepare chemically uniform substances, presumably methyl alcohol, a highly complex mixture was quite welcome to us, as its very complexity would make it more suitable as a motor fuel.

As to the composition of the products, our method yielded an aqueous liquor and an oily layer which contained hardly any hydrocarbons, whilst the B.A.S.F., according to their patents, chiefly find hydrocarbons. These circumstances, as well as the differences in raw materials and in the composition of the catalysts, make it desirable to give further details as regards the reaction products, particularly in view of the complete want of any scientific explanation of the process.

The liquid we obtained consisted broadly of an aqueous and an oily layer, mostly in the ratio of 2 : 1. The aqueous layer generally contained 20 per cent. of a mixture of aliphatic alcohols, aldehydes and ketones, in addition to free fatty acids, the main product being thus of an oily character. By working

our apparatus for several weeks, we have prepared larger quantities of these products for closer examination. Their genesis and the theory of the process, which are closely bound up with the knowledge of the many compounds formed, will be discussed at the end of this chapter.

(1) *Acids.*

We have demonstrated the presence of free acids in both the aqueous and oily layers. The aqueous layer was separated from the oil and rendered alkaline with caustic soda. Considerable quantities of iron hydroxide were precipitated. Alcohols, aldehydes and ketones, were distilled off in a Dufton<sup>182</sup> column. The remaining salt solution was acidulated with dilute sulphuric acid and submitted to steam distillation; the steam distillate was exactly neutralised with sodium hydroxide and evaporated to dryness on the water-bath. The salt residue was decomposed with sulphuric acid at 50°, and then exhaustively extracted with ether.

Acids were extracted from the oil by means of 5*N*-NaOH, and the oil was washed with water which also dissolved considerable quantities of non-acid constituents. The combined alkaline solutions were distilled in a column; the distillate consisted of an aqueous and an oily layer. The residue of sodium salts of the less volatile acids from the oil was decomposed with sulphuric acid, and the acids thus liberated were extracted with ether. This extract was combined with the ether extract of the water-soluble acids and dried with anhydrous sodium sulphate on a shaking machine; the ether was then distilled off with a Vigreux column. We thus obtained the fractions of Table LXXXI; the mean combining weights were determined by titration with sodium

TABLE LXXXI

Fraction.	Amount. g.	Mean combining weight.	Fraction.	Amount. g.	Mean combining weight.
100-117°	19.2	—	165-174°	6.3	—
117-119	7.1	62.4	174-176	3.3	100.0
119-140	24.3	65.2	176-185	2.9	—
140-142	11.8	74.0	185-187	6.9	116.0
142-153	5.6	—	187-204	7.1	—
153-155	10.5	82.5	204-206	7.3	146.8
155-162	3.1	—	Residue	7.4	—
162-165	11.6	88.9		134.4	

hydroxide. The identification of the individual acids, suggested by the titration, has been described elsewhere (*Brennstoff Chemie*, 1923, 4, 277).

The presence of formic, acetic, propionic and isobutyric acids was established.

To judge by the higher fractions and their combining weights, higher fatty acids are also present. Their identification was not attempted, but according to their combining weights and boiling points, they go up to  $C_8H_{16}O_2$ , showing a far-reaching building-up of acids from carbon monoxide.

(2) *Aldehydes.*

For a first orientation of the amounts of aldehydes present in the aqueous and oily liquids, use was made of reduction by means of ammoniacal silver solution. In the water-soluble alcohol-ketone mixture boiling below  $87^\circ$ , 2 per cent. of aldehyde, calculated as propionic aldehyde, was found. The steam-distilled oil was fractionated into 40 per cent. boiling below  $99^\circ$ , containing 7.2 per cent. of aldehyde, and 60 per cent. boiling above  $99^\circ$ , which contained 25.9 per cent. of aldehyde calculated as butyl aldehyde. The presence of propyl aldehyde and of isobutyl aldehyde was definitely proved; normal butyl aldehyde was probably present; formaldehyde was absent.

(3) *Alcohols and Ketones.*

The alcohol-ketone mixture, obtained by distilling the aqueous layer in a Dufton column, was dehydrated with lime and then fractionated. Table LXXXII gives the results after three fractionations.

TABLE LXXXII

Fraction.	Amount c.c.	Amount %.	Spec. grav.
53-58°	37.0	11.3	
58-64	23.3	7.1	
64-68	17.5	5.3	
68-73	29.5	9.0	
73-76	39.1	11.9	0.812
76-79	67.0	20.4	0.820
79-83	45.0	13.7	0.833
83-87	70.0	21.2	0.865

The fractions from  $72.5^\circ$  upwards still contained some water. Fraction 53-58° gave by a further fractionation 25 c.c. of boiling point  $55^\circ$ . The ultimate analysis showed this fraction to consist of about 80 per cent. of acetone and 20 per cent. of methyl alcohol; density  $D_4^{20} = 0.7977$ ; both compounds were isolated and identified.

In the higher fraction we suspected the presence of ethyl alcohol, isopropyl alcohol and methyl ethyl ketone. We isolated and analysed ethyl alcohol, normal propyl alcohol (not isopropyl alcohol); further, methyl ethyl ketone, diethyl ketone and methyl *n*-propyl ketone.

Other ketones were identified in the fraction of the steam distilled oil, boiling below 99°; these were diethyl ketone and methyl-*n*-propyl ketone.

(4) *Examination of the Oil.*

The oil, obtained from water gas in the high-pressure apparatus, leaves this apparatus as a clear yellow mobile liquid of a peculiar rather sweet smell. Separated from the aqueous layer and roughly dried through filter paper, it gave the following fractions :—

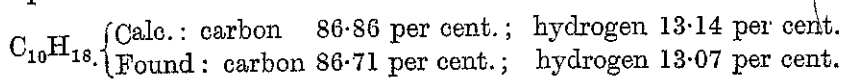
62–100°	150°	180°	200°
41	73	83	88 per cent.

Almost 90 per cent. of the oil thus boiled below 200°. Its specific gravity was  $D^{15} = 0.843$ . The fraction boiling below 100° contained 4 per cent. of alcoholic water.

To refine the crude oil (1450 grams), the acids were first removed by treatment with caustic soda. The oil was then washed with water, which dissolved about 10 per cent. of non-acid constituents. This aqueous solution gave on distillation with a column a distillate only partly miscible with water. These liquids have, therefore, a restricted solubility in water and go either into the aqueous or into the oil phase, according to proportions and solubility conditions. The crude oil, freed of acids and washed, was steam distilled; 943 grams of steam-distilled oil contained 5 per cent. of water, and 41.6 grams of non-volatile residue were obtained. The aqueous condensate contained a good deal of dissolved oil, which was fractionated from it through a column. The oil volatile in steam gave the following boiling ranges :—

40–100°	125°	150°	175°	200°	225°
40	63	77	87	92	96 per cent.

The oil was a yellow liquid of peculiar smell; the low-boiling fractions were colourless. Concentrated bisulphite solution dissolved 25 per cent. of the oil, and from this solution, on the addition of sodium carbonate, a colourless oil separated, the quantity of which did not agree with the observed diminution of volume. The oil insoluble in bisulphite was washed with sodium hydroxide and water to remove all bisulphite. The oil now had a pleasant smell, but it retained the original yellow colour. To test this oil for hydrocarbons it was diluted with ether and treated with metallic sodium. The sodium was dissolved with copious evolution of hydrogen, and alcoholates insoluble in ether were formed. The oil which had remained unattacked in the ether still contained, according to the ultimate analysis, 15.3 per cent. of oxygen. After four distillations over metallic sodium in a vacuum, the oxygen content was reduced to 0.22 per cent.



The hydrocarbons thus obtained amounted to 2.5 per cent. of the oil. Expressed in terms of the total steam-distilled oil, the figure would be 2 per cent., and it is not certain whether this small quantity was not the result of the treatment with sodium. There was not enough material for a closer estimation of the hydrocarbons. In any case, the hydrocarbons were quite minor constituents of the oil. As the B.A.S.F. state that their oil consisted chiefly of hydrocarbons, both saturated and unsaturated, their method of procedure must have differed essentially from ours. The preference of the B.A.S.F. for an excess of carbon monoxide over hydrogen, against our large excess of hydrogen, furnishes an explanation for the formation of hydrocarbons. It has been pointed out (p. 240) that carbon monoxide favours the scission of water from alcohols and the formation of olefinic hydrocarbons.

The oil was tested for esters by the determination of the saponification value. After 20 minutes' saponification under reflux with alcoholic potash, 1 gram of the steam distillate from the acid-free crude oil neutralised 4.7 c.c. of  $N/10$ -KOH, corresponding to a saponification number 26.3, or 4 per cent. calculated as acetic ester.

An estimate was finally made of the alcohol content of the oil. The fraction 99–225° of the steam distillate was shaken with bisulphite, which dissolved only 6 per cent. of the oil; in view of the previous findings, the bulk of the fraction soluble in bisulphite was therefore to be looked for in the fractions boiling below 99°. The oil, after washing with a sodium carbonate solution, was boiled under reflux with acetic acid anhydride for 1 hour; the blackish-brown product was treated for half an hour with boiling water in order to decompose the excess of anhydride. The oily layer was then washed with sodium carbonate, passed through a dry filter and distilled. The acetylated oil had the odour of amyl acetate, and gave the following fractions:—

86–99°	125°	150°	175°	190°
3	9	50	78	91 per cent.

Saponification with alcoholic potash yielded 28.9 per cent. of acetic acid.

If the molecular weight of hexyl alcohol is taken as a mean for the alcohols present, as justified by the boiling range of the oil and esters, the (hexyl) alcohol content works out at 50 per cent. of the oil. Renewed boiling of the acetylated oil with water convinced us that our method of preparation yields a product which is free of acetic anhydride. The water used for boiling contained very small quantities of acid, proving that undecomposed anhydride was not present, and that no appreciable saponification had taken place.

#### *Summary of the Reaction Products*

The individual compounds obtained in the pressure apparatus from water gas, and their relative quantities, are summarised in Table LXXXIII.



TABLE LXXXIII

Total amount of each group.	Identified so far.	Approx. quantity of identified compounds. % of total products.
10% acids.	Formic acid . . . . .	0.1
	Acetic acid . . . . .	2.3
	Propionic acid . . . . .	2.1
	isoButyric acid . . . . .	1.0
	Higher fatty acid up to C <sub>8</sub> . . . . .	4.5
29% water soluble alcohols, aldehydes and ketones.	Methyl alcohol . . . . .	1.5
	Ethyl alcohol . . . . .	14.5
	Propyl alcohol . . . . .	—
	Acetone . . . . .	5.2
	Methyl ethyl ketone . . . . .	—
11% oil partly miscible with water.		—
		—
48% oil volatile in steam.	Propionic aldehyde . . . . .	—
	Isobutyric " . . . . .	—
	Di-ethyl ketone . . . . .	—
	Methyl- <i>n</i> -propyl ketone . . . . .	—
	Higher alcohols up to C <sub>9</sub> . . . . .	15.0
	Ester . . . . .	2.0
2% oil not volatile in steam.	Hydrocarbons . . . . .	1.0
	—	—

The summary shows that the products represent an exceedingly complex mixture of diverse aliphatic compounds. The low-boiling constituents, such as acetone, methyl alcohol, and perhaps ethyl alcohol, are easily recoverable by fractional distillation so as to be available for chemical purposes or as solvents. The high-boiling constituents, which cannot be conveniently separated, will be useful as motor fuels.

#### (o) ROAD TESTS OF SYNTHOL <sup>181</sup>

Some road trials were made in order to test the suitability as motor fuels of the oil, called "Synthol" for short, obtained by the reduction of carbon monoxide in the high-pressure apparatus. For this purpose, the crude oil separated from its aqueous liquor was freed of acid and distilled in a fractionating flask up to 200°, when 87 per cent. of distillate was obtained. The bulk of the oil is, therefore, available as a light motor spirit. The constants of the oil thus obtained were :—

$$D_4^{20} = 0.8289$$

Carbon 69.29 per cent.; hydrogen 12.25 per cent.

Gross calorific value 8200 cal. per kg.

Nett calorific value 7540 cal. per kg.

Setting point: separation commences at  $-30^{\circ}$ , the liquid remaining mobile; complete solidification at  $-90^{\circ}$ . A 1:1 mixture of synthol and benzene remained clear down to  $-18^{\circ}$ , when separation set in.

Boiling range:—

62–80°	100°	120°	140°	160°	180°	200°
11	37	64	76	84	91	97 per cent.

The flash point of synthol is very low.

The running tests were conducted on a level road; in order to restrict the quantity of fuel required, a 4 h.p. N.S.U. motor cycle, model 1922, was used carrying two persons. The spirit was fed into the carburettor from a small funnel-shaped container. The speed was kept constant at 25 km. per hour. The trial runs were made with neat synthol, and with mixtures of synthol with benzol and benzol-alcohol. The carburettor was adjusted for benzol.

The distances run with 100 c.c. of spirit are tabulated in Table LXXXIV, which also states specific gravity and nett calorific values.

TABLE LXXXIV

Fuel.	Benzol.	Synthol.	Benzol-Synthol 1:1.	Benzol-Alcohol-Synthol 1:1:1.
Spec. grav. . . . .	0.879	0.829	0.854	0.840
Nett calorific value per kg. .	9570	7540	8580	7740
Nett „ „ per l. . . . .	8410	6250	7330	6500
Run in km. . . . .	2.9	3.0	3.2	2.9

Although synthol has a lower calorific value per unit volume than benzol, it gives more power. It is noteworthy that the mixture of benzol and synthol is still more efficient, showing that the calorific value is not the only determining factor, but that other properties of the fuel mixture must be taken into consideration. It has been suggested<sup>183</sup> that complex mixtures, having a regular boiling curve, are more suitable motor fuels than individual compounds or mixtures with broken boiling curves.

The engine started readily with synthol alone, and with the synthol mixture, and ran very smoothly. It would not run with 1:1 synthol-alcohol mixture. In the runs made with synthol alone, the exhaust smelled appreciably of synthol, obviously due to the jet being too large, which had been adjusted for benzol. With proper adjustment of the jet the result with synthol would be still more favourable.

Although the few trials were made merely to give an indication whether

synthol is at all suitable as a motor fuel, the mileage obtained shows that synthol is equal to benzol, if not superior to it, by virtue of such properties as its ability to bind water.

(p) CONVERSION OF SYNTHOL INTO SYNTHIN<sup>181</sup>

Synthol was freed of its constituents boiling below 99°, and the bulk boiling from 99° to 225° was then heated under pressure in an autoclave of 250 c.c. capacity, provided with an internal copper tube. After charging the oil, the air was removed by passing nitrogen in and blowing off. In one experiment 25 grams of oil were heated for 1 hour to 420°. After cooling, 2250 c.c. of gas were blown off, having the following composition:—

CO <sub>2</sub>	. . . .	14.5 per cent.	H <sub>2</sub>	. . . .	9.6 per cent.
C <sub>n</sub> H <sub>m</sub>	. . . .	22.7 ..	CH <sub>4</sub>	. . . .	21.8 ..
O <sub>2</sub>	. . . .	0.7 ..	N <sub>2</sub>	. . . .	16.1 ..
CO	. . . .	14.6 ..			

The absorption of the heavy hydrocarbons by sulphuric acid was sluggish and did not reach a constant value in several days; that part of the hydrocarbons which had escaped absorption would be included in the methane. The content of the autoclave (19 grams) consisted of two layers, a dark reddish-brown oily layer (17.5 c.c.) and an aqueous liquid (3.5 c.c.).

In a second experiment \* 40 grams of oil were heated for 1 hour to 450°. We obtained 3550 c.c. of gas, and 27.1 grams of liquid products, the oily layer amounting to 27 c.c., the aqueous to 4.5 c.c. A third experiment was made under the same conditions, and the reaction products of the three experiments were united. The water was separated and the oil was fractionated, giving the following boiling range:—

Below 50°	75°	100°	125°	150°	175°	200°	225°	250°	275°	300°
4	10	17	22	35	48	57	65	74	78	84 per cent.

The fractions boiling below 100° had the smell of benzene and coloured sulphuric acid only slightly, except the fraction 75–100°; this fraction was refined with sulphuric acid and distilled.

Of the united fraction boiling above 100°, 50 per cent. was soluble in concentrated sulphuric acid.† The portion insoluble in H<sub>2</sub>SO<sub>4</sub> was washed with water and alkali, and then steam-distilled. The distillate had a pronounced petroleum smell. It was submitted to fractionation and yielded:—

120–150°	150–200°	200–270°	Above 270°
24	44	27	5 per cent.

\* It is interesting to compare heating of synthol in the autoclave and at ordinary pressure. If synthol is distilled through an iron tube at rising temperature, slow decompositions set in at 400°. At 450° the decomposition is very brisk, synthol dissociating into hydrogen, carbon, some carbon dioxide and methane. At 480° no more liquid is left, but only carbon and gas.

† Synthol is almost completely soluble in concentrated H<sub>2</sub>SO<sub>4</sub>.

The fractions insoluble in concentrated sulphuric acid proved to be hydrocarbons of the following composition and density :—

TABLE LXXXV

Fraction.	% C.	% H.	C : H. ratio.	D <sub>4</sub> <sup>20</sup> .
Below 50°	84.12	15.44	1 : 2.19	—
75–100	84.48	15.14	1 : 2.13	0.762
120–150	86.89	13.37	1 : 1.83	0.778
150–200	87.74	12.67	1 : 1.72	0.818
200–270	88.43	12.05	1 : 1.62	0.874

A portion of the product of heating under pressure dissolved in sulphuric acid, but separated on dilution with water as oil; this was washed in the customary way and steam-distilled. The steam distillate gave the following fractions :—

100–175°

33

175–235°

54

Above 235°

13 per cent.

The main portion boiling between 175° and 235° contained carbon 79.05 per cent. and hydrogen 11.20 per cent., and, therefore, still contained oxygen.

The bulk of the alcohols, aldehydes and ketones making up synthol can, therefore, be converted into a product in which hydrocarbons predominate. Some of these boil at lower temperatures than the raw material; some have higher boiling points, are not attacked by sulphuric acid, and are saturated. The ultimate analyses show that the C : H ratio increases with rising boiling points. In the lowest-boiling fractions the C : H ratio is about 1 : 2, as in simple naphthenes; the higher-boiling fractions must consist of saturated hydrocarbons built up of several condensed-ring groupings. The process possibly takes place in two stages. In the first, the alcohols split off water to yield the corresponding olefines, fragments of which then reunite, as in the experiment of Ipatiew,<sup>184</sup> under the influence of pressure to naphthenic hydrocarbons. This view was supported by the high olefine content of the gas, and by the fact that lighter and higher boiling hydrocarbons are formed than could be expected from a simple conversion of alcohols into the corresponding naphthenes.

#### (g) FORMATION OF PETROLEUM FROM WATER GAS

The transition of synthol constituents into hydrocarbons of the petroleum type raises the question of an analogous genesis of mineral oils and, as a special case, the theory of inorganic petroleum formation. The primary conditions for a formation of natural oil from water gas is the occurrence of carbonaceous matter in the lower strata of the earth. Contrary to Moissan's hypothesis, it is immaterial for the synthesis from water gas whether it is in the form of

free carbon or carbides. There is ample evidence of the presence of carbon at low depths, and it is manifest that steam penetrating into them would form water gas with the carbonaceous material, or, at somewhat lower temperatures,  $\text{CO}_2$  and hydrogen. The escape of such gases from fissures in the earth has actually been observed in volcanic districts. La Croix and Giraud, in 1902, collected the gases issuing from a surface fumarole at Mont Pelé, which Moissan analysed and found to contain:  $\text{O}_2$  13.67 per cent.,  $\text{N}_2$  54.94 per cent., A 0.71 per cent.,  $\text{CO}_2$  15.38 per cent.,  $\text{CO}$  1.60 per cent.,  $\text{CH}_4$  5.46 per cent., and  $\text{H}_2$  8.12 per cent. The figures indicate that quite two-thirds of the gas consisted of air. A calculation, eliminating the air constituents O, N, and A, gives,  $\text{CO}_2$  50.3 per cent.,  $\text{CO}$  5.2 per cent.,  $\text{CH}_4$  17.8 per cent., and  $\text{H}_2$  26.7 per cent. We have frequently observed similar mixtures as the residual gas of synthol preparation; for example, in Expts. 93, 139 and others. It is, moreover, possible to produce from a gas of this composition more synthol by contact with iron and bases at about  $400^\circ$ , and under pressure. All the necessary conditions are found in the interior of the earth.

Ramsay<sup>185</sup> has been at pains to establish the presence of traces of nickel in all petroleum as a proof of its formation by catalytic hydrogenation from acetylene, according to Sabatier. This postulate seems hardly called for, since it has been shown in this book that the formation of "synthol," and its conversion into "synthin" takes place most readily in contact with iron. With the knowledge of the occurrence of carbon in the earth's crust, and of water gas emanation in volcanic districts, no further assumptions are needed for admitting the possibility of petroleum formation by a "synthol" process.

Leaving aside Engler's hypothesis of an organic origin of petroleum, the two inorganic theories, *i.e.*, the direct formation of petroleum from carbides (Mendelejeff and Moissan) and the indirect formation *via* acetylene (Sabatier and Senderens), may now be supplemented by the equally feasible "synthol" theory (Fischer and Tropsch). The hypothesis of an inorganic genesis has recently again found advocates.<sup>186</sup> In view of the possible formation suggested, and of the diverse composition of crude oils (paraffinoid, naphthenic and partly aromatic), the need of tracing all occurrences of liquid hydrocarbons in the earth's crust to a single genetic principle does not exist any longer. Every case will have to be considered on its merits. An important point with a petroleum of biochemical origin is the certainty of exhaustion of the deposit. For mineral oil of Plutonic origin, the expectation of life is very different.

#### (r) ATTEMPT AT AN EXPLANATION OF THE SYNTHOL PROCESS

##### 1. *Experimental Conditions which a Theory must Fit*

Any explanation of the result described must pay due regard to two facts. The experiments performed with numerous metals, other than iron, have

demonstrated that only those base metals are active which are known as hydrogen carriers, that is, besides iron, nickel, cobalt, and, in a very slight degree, manganese.

The formation of alcohols, oil and the like is successful only when, in addition to these metallic hydrogen carriers, bases and their salts with weak acids are present, and it would appear that the efficiency of oil production depends on their strongly basic character. The base alone, for example, KOH on pumice, is not sufficient; a hydrogen carrying metal must be present.

In contact with iron at a temperature of about 400° under pressure, water gas is converted into a mixture of methane and carbon dioxide (as shown in a previous paper).<sup>187</sup> In the presence of such bases or salts the formation of methane decreases and liquid products appear.

### 2. *Formation of Formaldehyde*

It may be assumed in all cases of contact with metallic hydrogen carriers that, in the first instance, hydrogen combines with carbon monoxide with formation of formaldehyde. The possibility of this reaction at atmospheric pressure has been demonstrated by Jaeger and Winkelmann.\* In experiments made with water gas under pressure, in which liquid products were at once condensed on the hot and cold tube principle, Fischer and Jaeger\* obtained considerable quantities of formaldehyde. In the present experiments the formaldehyde has undergone further changes. In the absence of bases or suitable salts, 2 molecules of formaldehyde may be converted into 1 molecule of carbon dioxide and 1 molecule of methane, according to the equation:  $2\text{CH}_2\text{O} = \text{CO}_2 + \text{CH}_4$ ; <sup>183</sup> or the reduction to methane may proceed further with formation of 1 molecule of water, which, reacting in its turn with carbon monoxide, yields hydrogen and carbon dioxide. The two possible ways of methane formation lead to the same result, 1 molecule of carbon dioxide being produced for each molecule of methane.

### 3. *Modification of the Reaction*

In the presence of the bases or salts, the secondary change of formaldehyde may proceed in another way. The investigations of Tropsch and Roelen\* have demonstrated that formaldehyde in the presence of sodium carbonate is readily transformed into methyl alcohol at 400° and at ordinary pressure; 2 molecules of formaldehyde yielding 1 molecule of methyl alcohol and 1 molecule of carbon monoxide.

It may be presumed that formaldehyde produced under pressure will also be converted into methyl alcohol by bases and their salts with weak acids, reduction of carbon monoxide under these conditions resulting in the formation of the alcohol, instead of methane and carbon monoxide. An experiment in which para-formaldehyde was vaporised in a current of water gas under a pressure

\* Unpublished.

of 100 atm., and the vapours were passed over pumice impregnated with potassium carbonate at 400°, yielded large quantities of methyl alcohol.

#### 4. *Synthesis by Condensation of Aldehydes*

Whilst there is little doubt as to the primary formation of formaldehyde, and the possibility of directing its transformation or further reduction, the synthesis of butyl alcohol, for example, leaves room for speculation along various lines. In the circumstances, formaldehyde may be directly condensed to larger compounds, analogous to aldol condensation, which is known to be especially favoured by the presence of alkali. Reduction may take place at the same time.

#### 5. *Synthesis by Carbon Monoxide Addition to Alcohols*

Just as carbon monoxide combines with water to formic acid, it might unite with methylated water, *i.e.*, methyl alcohol, to give acetic acid. Suggestions to that effect have been made by Geuther,<sup>189</sup> who, by the action of carbon monoxide upon sodium ethylate at 190°, obtained sodium propionate. There is also a statement by Ljubawin<sup>190</sup> that ethyl acetate heated in a sealed tube in the presence of calcium oxide gave butyric acid as chief product. The statement is interesting, as it is conceivable that carbon monoxide and alcohol do not at once combine to form acids but alkyl formates,<sup>191</sup> which subsequently are transformed into acids by their contact with our alkaline catalyst.

On the assumption that acetic acid is formed from methyl alcohol, either directly or via methyl formate, it is not difficult to explain the appearance of acetaldehyde and ethyl alcohol by progressive reduction of acetic acid under the catalytic influence of the metallic hydrogen carrier. Nor is there any objection to explaining the occurrence of acetone by the catalytic decomposition of acetic acid on the bases or salts of the contact substance,\* or the conversion of acetone into isopropyl alcohol by an addition of hydrogen.

Consistently following up the life-history of ethyl alcohol produced by the reduction of acetic acid, the formation of propionic acid by addition of carbon monoxide, and of propyl aldehyde and *n*-propyl alcohol by reduction of the former, must be admitted. That di-ethyl ketone may catalytically result from propionic acid, or that methyl ethyl ketone may be formed from 1 molecule of propionic acid and 1 molecule of acetic acid, is evident, as is also the formation of the corresponding iso-alcohols by addition of hydrogen to these ketones. The appearance of all the products found can be easily explained on the same lines.

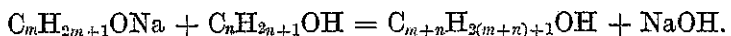
The analysis of the oily products indicated that condensation does not proceed very far but is limited to 7 or 8 carbon atoms; at temperatures of 400° and above, the higher members of the aliphatic series are no longer stable, as is known from the cracking of high-boiling into low-boiling hydrocarbons.

\* A portion of the bases of the used catalyst is always found to be combined with acetic, propionic, butyric acids, etc.

The conditions in Geuther's and Ljubawin's experiments are cited in elucidation of the direct and indirect formation from alcohols of acids rich in carbon; these conditions, *i.e.*, entire absence of water, do not obtain in our apparatus. The high pressure under which we work may so much favour the condensation which takes place with diminution of volume, that the presence of steam does not interfere as it would at ordinary pressure. The attempts of von Philippovich\* to prepare alcohol and oil at ordinary pressure with the aid of the identical iron-potassium carbonate catalyst failed entirely. High pressure is indispensable for this reaction, as is easily understood on considering that the addition of carbon monoxide to alcohol diminishes the number of molecules to one-half.

#### 6. *Synthesis of Higher Alcohol by Dehydration*

Guerbet,<sup>192</sup> on heating sodium or barium alcoholates for some time with alcohols under pressure to 200° or 250°, observed a scission of water and the formation of higher alcohol, in accordance with the equation:—



In this way he synthesised quite a number of higher alcohols from the lower, *i.e.*, *n*-butyl alcohol, 2-methyl-pentanol-1, dibutyl alcohol, etc., but did not succeed in condensing methyl alcohol to ethyl alcohol, as, owing to the pressure set up by the decomposition of methyl alcohol, sealed tubes always burst. Repeating Guerbet's experiment with methyl alcohol in a steel autoclave, we obtained, after 24 hours' heating to 240°, dimethyl ether in considerable quantities. At higher temperatures (400° to 430°), in the presence of alkali-iron catalyst, higher-boiling oily products resulted. The decomposition of methyl alcohol into hydrogen and carbon monoxide proceeded, however, too far to be quoted in support of our explanation; for it is conceivable that the higher-boiling products obtained with the aid of the catalyst are formed from the gases liberated by the very mechanism of the reaction which we are trying to explain.

Like Geuther, Guerbet worked with dry alcoholates in the absence of water. The same considerations apply to Guerbet's experiments in explanation of the building-up of higher alcohols from lower ones in our contact apparatus, as to those of Geuther. The assumption would have to be made that the reaction, which at low pressure takes place only in the absence of water, would at high pressure be possible in the presence of water.

#### 7. *Other Possible Explanations*

Without wishing to decide as yet in favour of any one of the suggested interpretations, since several modes of formation may run concurrently,†

\* Unpublished.

† A synthesis by reduction of iron carbonyl with liberation of iron is not likely, although iron, nickel and cobalt form carbonyls.



synthesis by addition of carbon monoxide to alcohols seems to be the most lucid and consistent. It would imply building-up only, and not regeneration of hydrogen, such as would have to be postulated for a formation of acids by the action of alcohols upon the salts in the catalyst, with loss of hydrogen after the manner of Hell's reaction, or for the formation of acetone by the scission of hydrogen from previously formed isopropyl alcohol.

An explanation involving the reduction of carbon monoxide down to a  $\text{CH}_2$ -group, the union of such groups to olefines, and the hydration of olefines to alcohols seems hardly probable; to account for the aldehydes and acids found, a scission of hydrogen would have to be admitted, which, in view of the tendency to hydrogen addition in operations taking place under high hydrogen pressures, is very unlikely. If olefines were built up of  $\text{CH}_2$ -groups, one would rather expect any hexylene formed to be hydrogenated to hexane. As a matter of fact, we have found practically no liquid hydrocarbons in these reactions.

It was originally intended to work out a continuous process for the recovery of products which are obtained by preparing formates from carbon monoxide, and by the thermal decomposition of these formates, *e.g.*, lithium formate. In the first experiments, the apparatus had been charged with lithium carbonate on pumice, in the hope that the alternate formation and decomposition of lithium formate might lead to liquid reaction products of carbon monoxide. The experiments were later repeated with potassium hydroxide on pumice. It was found, however, that the desired effect could not be realised in the absence of metallic hydrogen carriers. For these reasons the reactions taking place in our apparatus cannot be explained simply by the intermediate production of formates.

We may conclude this section on the theory of synthol formation by stating that a synthesis by addition of carbon monoxide to alcohols appears, for the present, to be the preferable explanation of the reaction, but we do not claim to have proved this hypothesis definitely.

In presenting this account of our results we have spoken of "synthol" in order to avoid the reiteration of references to "mixtures of reaction products insoluble or not readily soluble in water, and consisting of alcohols, ketones, aldehydes, etc." We recognised that we had not to deal with a uniform chemical compound, nor with a definite class of compounds. The term is employed merely to indicate synthetic substances of an oily character. In justification of our claim to a name for this mixture we may point out that we have been able to elucidate its composition, which differs materially from that of the products obtainable by the process of the B.A.S.F.; the latter consist, according to the statements of the B.A.S.F., predominantly of hydrocarbons, which are obtained only in minute quantities by our method. We have further ascertained that the water-soluble products, methyl alcohol, ethyl alcohol, propyl

alcohol, and acetone, represent the preliminary stages in the formation of the oily substances, not soluble in water, of "synthol" proper. The water-soluble mixture we propose to call "*pro-synthol*."

Later researches have shown that synthol, heated in an autoclave in the absence of carbon monoxide, and therefore excluding the possibility of its further addition, is by dehydration converted to a large extent into a mixture of hydrocarbons of pronounced petroleum smell. In that reaction the higher alcohols are probably transformed with loss of water into olefines, and further, by the closing of rings, into naphthenes. Synthol thus transformed into petroleum or benzine we propose to name "*synthin*." The genetic sequence of the building-up of our compound from carbon monoxide would therefore be: *pro-synthol*, *synthol*, *synthin*. The first and second contain oxygen; the third is free of oxygen, or contains, if not entirely converted, less oxygen.

Much further work will be needed before the technical production or manufacture of synthol is so far improved as to reach the economic stage. We believe, in view of the progress we have made in demonstrating its possibility, that a rational method of converting coal—which, if sufficiently bituminous, would first be deprived of its primary tar—by gasification into water gas, and finally into synthol and low-boiling motor fuels, would be of far-reaching importance generally, and particularly for countries which possess coal but no petroleum. The working scheme would be: coal, semi-coke, primary tar, primary benzine and gas; from the semi-coke, water gas, ammonia, and hydrogen sulphide; from the water gas, *pro-synthol*, *synthol*, and eventually *synthin*.

#### (s) INDUSTRIAL APPLICABILITY OF THE SYNTHOL PROCESS

The Haber synthetic ammonia process, as carried out on the very largest scale at Oppau and Merseburg, seems to furnish the best basis for a comparative consideration of the pressures, temperatures and other factors which the industrial application of the synthol process would necessitate. The technical difficulties of the synthol process are, without doubt, smaller than those of the ammonia process, though it appears much more complex in regard to products. The two components of the Haber reaction, nitrogen and hydrogen, yield only one product, ammonia; in the synthol process, three components, carbon, hydrogen and oxygen, may yield perhaps 100 different compounds. The temperatures required are lower by 200°, being 410° instead of 600°, a point of great importance for the construction of the contact tubes. Not only the temperature, but the composition of the gas makes for greater durability of the contact tubes. According to statements in the technical literature, the hydrogen in the Haber process has an undesirable effect on the steel of the tube, in that it dissolves carbon from the steel in the form of methane and combines with the soft iron thus produced to a brittle hydrogen-iron alloy, of low tensile

strength. Special measures had to be devised to circumvent this difficulty. Whether it is really hydrogen, and hydrogen alone, which causes the brittleness of the steel in the Haber process, remains to be seen. It is conceivable, though this has not been suggested in the literature, so far as I am aware, that the brittleness of the steel is due to ammonia itself and to the formation of iron nitride. The best temperature for the formation of iron nitride (which in a pure state has the appearance of white firebrick) from ammonia and iron lies between  $450^{\circ}$  and  $475^{\circ}$ . At atmospheric pressure ammonia acts even above  $475^{\circ}$  on iron with formation of nitride, and it is therefore possible that the reaction at high pressure still takes place at  $600^{\circ}$ .

However that may be, nitride formation is out of the question with the gas mixture of the synthol process. The risk of a deleterious action of hydrogen is counteracted by the presence of carbon monoxide which has a carburising action on the steel. This argument is supported by the fact that with water gas at  $410^{\circ}$  we have never observed our steel tubes to get brittle, though keeping them in use for years. Nor was any hardening effect found in reboring the tube.

It would thus appear that the construction of apparatus for the synthol process is less difficult than that for the Haber process, since the deposition of carbon in the contact tube has been successfully suppressed, and the pressures are not so high.

*Gas Supply.*—A suitable gas for synthol manufacture is water gas; producer gas is also applicable, as well as blast-furnace gas or carbon monoxide, mixed with steam. An excess of hydrogen \* being advantageous, it is advisable to add hydrogen or coke-oven gas to water gas; a proper gas mixture may be made directly by steaming in coke-ovens. If it is not desired to mix other gas with water gas, an excess of hydrogen over carbon monoxide may be secured by using a water gas rich in carbon dioxide, and scrubbing out the latter. Another alternative, which is probably preferable, is to admix steam with water gas and catalytically convert some carbon monoxide into hydrogen and carbon dioxide, which latter is washed out; or else part of the water gas may be thus treated, and the residual hydrogen added to another part. The removal of the carbon dioxide may be effected in various ways, the most efficient being washing out with water under pressure.<sup>169</sup>

If gases containing nitrogen, such as ordinary producer gas and blast-furnace gas, are used, higher compression must be applied in order to attain the

\* The advantage lies partly in the prevention of carbon deposits. The chief point is that the gas originally contains as much hydrogen as corresponds to the composition of synthol. If one imagines the elements of water to be split off from the alcohol and ketones in synthol, the ratio of the residual carbon to hydrogen would be 1 C : 2 H. To convert water gas completely into synthol, alcohol and water, it should be so enriched with hydrogen that there are 2 parts of hydrogen to 1 part of carbon, as if the intended reaction were:  $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ . Besides, it appears more advantageous that the oxygen of carbon monoxide, which does not enter into the synthol, should form  $\text{H}_2\text{O}$  and not  $\text{CO}_2$ , as in form of water it can be eliminated by simple condensation between two successive contact tubes.

same absolute pressure of carbon monoxide, as it should have in gas free of nitrogen.

It need hardly be said that for the production of the water gas any solid fuels are utilisable, such as coal, peat, wood, and their carbonising residues.\* This fact imparts a certain independence to the synthol process, as it can be carried on where cheap power can be obtained, some kind of fuel being available almost anywhere. Even natural gas is applicable, as it readily yields the necessary hydrogen, carbon monoxide and carbon dioxide.

Since one may start from carbon dioxide instead of carbon monoxide, provided hydrogen be available, yet another variant is to produce hydrogen electrolytically and to extract carbon dioxide from flue gases, or lime-kiln gas, or even from the atmosphere. If an economical method could be developed by which carbon dioxide is washed or frozen out of air, it should be feasible in districts where cheap water power is available, or with some future form of energy, to manufacture synthol after the manner in which Nature has built up fuels using atmospheric carbonic acid as raw material and light as the source of energy.

*The Supply of Energy.*—Since the formation of synthol liberates energy, in large contact apparatus some heat would probably be required for starting-up but very little for running. Some cheap source of energy must be found for compressing the gases. A small portion of this energy would be recoverable by expansion of the unconsumed gas, but the process should be initiated with such gas mixtures and so conducted that the conversion is fairly complete, leaving little energy to be recovered. In view of the various possibilities of treating the problem, it is purely a question of economics whether the compression energy should be generated in coal-power or in water-power plants, whether coke should be transported to water-power stations or electric energy transmitted to the fuels at their source of origin, or whether finally, what seems the most reasonable course, energy and raw material should be produced in the coal-fields. The compression energy might also be derived from the spare power of large coal-burning power stations during light-load periods. Water gas, accumulated in ordinary gas holders, might be compressed during such periods into high-pressure storage tanks from which the contact plant would be supplied in a continuous process. The discontinuous operation of ordinary water gas plants is a disadvantage. The continuous electric water-gas generators<sup>193</sup> of Stassano may deserve attention in this connection.

\* It is interesting in this connection to compare the hydrogenation of coal with synthol formation. The former succeeds best with geologically young coals and by hydrogenating causes degradation from large to smaller molecules. In the case of synthol, the nature of the fuel is immaterial. As gasification always starts from the carbonising residue, the youngest coal will serve as well as the oldest. Further, synthol is built up by small molecules growing into larger molecules. Thus the low-boiling compounds are first produced and from these the liquid fuels of high boiling range; the latter result only in so far as they are still stable under the conditions of their formation.

## CHAPTER V

### HYDROCARBONS FROM CARBIDES

THERE is yet another way for the direct or indirect conversion of coke into liquid hydrocarbons, not depending upon gasification of coke and catalytic treatment of the water gas produced. By thermal processes, carbides can be obtained from coke and suitable oxides or metals, to be subsequently decomposed. Moissan divided the carbides into two groups: (1) Carbides which yield hydrocarbons by decomposition with water, and (2) Carbides which are *not* decomposed by water alone. To the former class belong the carbides of the alkalis, the alkaline earths, of beryllium, aluminium, manganese and uranium, and the carbides of the rare-earth metals.

The carbides of the other metals are not decomposed by water under ordinary conditions, but some yield hydrocarbons when treated with dilute acid. Some of the carbides decomposable by water generate only one kind of hydrocarbon, either acetylene or methane. Other carbides do not evolve a uniform gas, but a mixture of different gaseous hydrocarbons, and, in addition, frequently liquid and solid hydrocarbons. From such carbides free hydrogen and carbon is occasionally separated.

One of the carbides which, decomposed with acids, evolve liquid and solid hydrocarbons, is uranium carbide. Some other less costly carbides yield liquid hydrocarbons; even the iron carbides present in iron and steel do so when treated with acids. Though there is so far no indication of a practical method of producing liquid hydrocarbons from metallic carbides, reference to the theoretical possibilities must be made in the concluding chapter of this book. These possibilities include the production of carbides which directly generate liquid hydrocarbons, and the indirect method of converting acetylene and methane, the gaseous decomposition products of carbides, into liquid hydrocarbons.

#### (a) CARBIDES WHICH DIRECTLY YIELD LIQUID HYDROCARBONS

Manganese carbide, prepared in the electric furnace from  $\text{Mn}_3\text{O}_4$ , generates with water a gas consisting of methane and hydrogen.<sup>194</sup>

Attempts to prepare a double carbide of calcium and manganese which might yield acetylene, methane, and hydrogen, have been unsuccessful.<sup>195</sup>

By heating powdered manganese metal in a current of methane (not a practical proposition) very high-carbon carbides can be prepared. Dissolved in dilute acid, such carbides containing more than 8 per cent. of carbon leave fatty or paraffin-like hydrocarbons and spongy carbon. Hilpert and Paunescu,<sup>196</sup> who have experimented in this direction, suggest that these respective manganese carbides do not contain single molecules, but polymerised molecules of long carbon-chain structure.

That the dissolution of ordinary iron containing some carbon does not yield pure hydrogen has long been known from the peculiar odour of the gas. It has further been demonstrated that in the decomposition of iron carbide, isolated from steel, more than half of the carbon may occur as gaseous hydrocarbons. These hydrocarbons are partly saturated and partly unsaturated compounds, the latter consisting mainly of butylene.<sup>197</sup> A small quantity of liquid hydrocarbons is always observed, but statements differ as to the presence of free carbon.

Mylius, Foerster, and Schöne<sup>198</sup> found that in the decomposition of iron carbide by acids, 100 volumes of the gas evolved contained a quantity of hydrocarbons equal to 15.3 volumes (calculated as gaseous carbon). Decomposition of iron carbide by steam or superheated water did not yield hydrocarbons but hydrogen, an observation of some importance for technical developments. For commercial purposes decomposition of iron carbides, or highly-carburised iron, only by water or steam, but not by acids, can be considered. All investigations, though differing as to details, indicate that iron carbide on decomposition yields negligible proportions of liquid, and mainly gaseous hydrocarbons. A statement in the literature<sup>199</sup> that the carbon in iron carbide forms predominantly "liquid" products is due to an obvious misprint, "fluid" instead of "volatile" ("flüssige" instead of "flüchtige"), as shown in a later paper by the same authors,<sup>200</sup> which speaks of volatile hydrocarbons as predominating. This statement is in accord with the observations of other workers. According to Hilpert and Dieckmann,<sup>201</sup> there are, in addition to  $\text{Fe}_3\text{C}$ , the carbides  $\text{Fe}_2\text{C}$  and  $\text{FeC}$ , formed by the action of carbon monoxide upon iron oxide or upon  $\text{Fe}_3\text{C}$ . On dissolving these very stable carbides in hydrochloric acid, large quantities of fatty substances are formed; the gases evolved are chiefly hydrogen and a little methane.

Schenck, Giesen, and Walter<sup>202</sup> have recently published a paper on the decomposition of metallographically well-defined iron and manganese carbide alloys. Determining the hydrocarbons, qualitatively and quantitatively, and establishing a carbon balance between the iron carbide and the products of reaction, they arrive at the figures of Table LXXXVI.

Among the gaseous hydrocarbons propylene and butylene predominate to a striking extent. The liquid hydrocarbons, hexene and octene, are present in minor proportions. The large amount of residual carbon is very curious. When the ferrous chloride solution was continually withdrawn and replaced by fresh acid, the iron carbide was dissolved with complete hydrogenation of the carbon. According to Schenck, deposition of carbon occurs when ferrous chloride is allowed to concentrate in the acid, as then the potential difference between the iron and the iron solution is changed so that the hydrogen liberated has a diminished reducing power.

TABLE LXXXVI

Hydrocarbons.	Alloy 2. Cast iron 2.5% C. Cementite, Ferrite.	Alloy 3. Steel 1.7% C. hardened at 1150°. Cementite, Austenite, Martensite.	Alloy 4. Steel 1.7% C. hardened at 780°. Cementite, Martensite.
1. Methane . . . .	1.02	3.53	3.19
2. Ethane . . . .	0.10	0.50	0.45
3. Ethylene . . . .	0.27	0.50	0.47
4. Propylene . . . .	7.08	24.37	25.21
5. Butylene . . . .	4.00	10.25	9.08
6. Amylene . . . .	1.25	3.36	4.20
7. Hexene . . . .	1.15	4.37	5.21
8. Octene . . . .	0.80	3.02	3.36
9 Carbon . . . .	78.04	38.82	42.10
Loss . . . .	6.29	11.28	6.73

Another explanation of the appearance of long-chain hydrocarbons assumes the pre-existence of these chains in the iron carbides. Schenck inclines to the view that the hydrocarbons are formed by interaction between nascent carbon and nascent hydrogen.

The study of the conditions under which hydrocarbons, and particularly liquid hydrocarbons, are formed in the decomposition of the iron carbides is undoubtedly of importance; it might indicate the best conditions under which decomposition should be effected. For the present, the yields of liquid hydrocarbons from carbides are too small, and even if they should be capable of considerable improvement, their production would only acquire practical importance if decomposition could be effected by means of steam. In that case, the hydroxide formed might be reconverted into carbide by means of carbon monoxide, and the process might then become a commercial proposition. Those possibilities are, however, remote.

The carbides which give better yields of liquid hydrocarbons are unfortunately very expensive, and will, therefore, be noticed very briefly. Among these are the carbides of cerium, lanthanum, samarium, thorium and uranium. Uranium carbide can be decomposed by water. The gases consist of 15 per cent. of hydrogen, 78 per cent. of methane, 7 per cent. of ethylene and a fraction of 1 per cent. of acetylene; they represent only one-third of the carbon content of the carbide, the other two-thirds remain in the residue as liquid or solid hydrocarbons. By the expense of regenerating uranium carbide from the oxide, and the high cost of uranium minerals themselves, this process is doomed to failure.

## (b) CARBIDES GIVING HYDROCARBONS WHICH CAN BE CONVERTED INTO LIQUIDS

Calcium carbide, which is the best known of all the carbides and the only one manufactured on a very large scale, yields acetylene on decomposition with water. Pure acetylene is generated by the carbides of the alkali and the alkaline earth metals. Magnesium has been stated to form a second carbide yielding allylene.<sup>203</sup> That acetylene is transformed into tarry products containing benzene, when passed through tubes at red heat, was shown by Berthelot.<sup>204</sup> The reaction according to the equation  $3C_2H_2 = C_6H_6$  looks very simple. In reality the reaction does not proceed either exclusively or predominantly in this sense. In order to suppress the strong soot formation which accompanies it, Richard Meyer<sup>205</sup> diluted acetylene with an equal volume of hydrogen and effected decomposition in electrically and uniformly heated tubes at a temperature between 640° and 650°. Much carbon was still deposited; the tar represented not more than 60 per cent., and the benzene 12 per cent. of the weight of acetylene. The conversion of acetylene into benzene gives, therefore, a decidedly low yield. Other experiments<sup>206</sup> in this direction, aiming at more favourable conditions, were not more successful, and, for the present, calcium carbide cannot be considered a suitable raw material for the economical production of benzene by an indirect method.

This opinion is little affected by the experiment of Tiede,<sup>207</sup> who, working at 610° and taking particular care to keep the temperature constant, obtained about 40 per cent. of oily products from acetylene. A good catalyst was not discovered, and the same results were obtained without catalysts. About 50 per cent. of the oil fractions boiled between 50° and 150°, and 15 per cent. between 150° and 200°. Referred to the acetylene consumed, the results are not much better than those of Richard Meyer.

More recently N. Zelinsky<sup>208</sup> has shown that the polymerisation of acetylene to benzene takes place with a much better yield if the acetylene, adsorbed by activated carbon and thus highly condensed, is exposed to a temperature of about 600°. He then succeeded in obtaining 70 to 74 per cent. by weight of the acetylene as a light tar, half of which boiled below 150° and contained about 35 per cent. of pure benzene. Referred to the acetylene used, the yield of crude benzol, boiling below 150°, would be 35 to 37 per cent., and that of pure benzene 25 per cent. These yields are approximately twice as high as those of Meyer, but still represent only a quarter of the theoretical. The higher-boiling products contain toluene, xylene, styrene, indene, naphthalene, fluorene, and anthracene. One hundred parts of acetylene tar yielded the fractions: 20° to 150°, 45 per cent.; 150° to 250°, 14 per cent.; above 250°, 29 per cent.; residue, 12 per cent.

The amount of liquid motor fuel would, in the most favourable case, be



$45 + 14 = 59$  per cent. of the tar, or about 40 per cent. of the weight of acetylene used.

More favourable yields have been realised by the action of the silent electric discharge,<sup>209</sup> which polymerises acetylene quantitatively to an oily substance. But this oil is exceedingly unstable; exposed to the air it absorbs oxygen avidly. Out of contact with air, the oil becomes progressively more viscid, and after a few days it forms a very hard brittle mass. For practical purposes this mode of preparing oil from acetylene may, therefore, be excluded.

Another possibility of producing liquid hydrocarbons from acetylene was described by Sabatier.<sup>164</sup>

If acetylene mixed with double its volume of hydrogen is passed over finely divided reduced nickel, some carbon is deposited, the mass heats spontaneously, and gaseous and some liquid saturated hydrocarbons are produced. With a smaller excess of hydrogen more liquid hydrocarbons are obtained, whilst the spontaneous heating of the nickel is more intense. The hydrocarbons obtained in the latter case are partly hydroaromatic and partly aromatic. This hydrogenation of acetylene, according to Sabatier, does not seem promising for the practical manufacture of liquid fuels.

There remains, finally, the possibility of utilising the carbides which generate methane. So far, nothing is known in regard to the transformation of methane with loss of hydrogen into liquid hydrocarbons, though the problem, given suitable conditions, cannot be dismissed as impossible. If such a method could be found, it would appear to be more advantageous to prepare the methane by the reduction of carbon monoxide than from carbide. Methane from coke-oven gas and the fire damp from coal mines, and above all of natural gas, could then be pressed into service.

Reviewing the practical possibilities of obtaining liquid fuels by way of carbides, the conclusion forces itself upon one's mind that the future of this field of research remains as yet entirely obscure.

Of the various methods for the conversion of coal into oil which have been examined in this book, primary tar production, followed by rational working-up of the tars, and combined with preparation of synthol from semi-coke and water gas, would appear to be the most promising. I do not wish to conclude without pointing out that I have purposely limited myself to describing the more recent processes in course of development, or capable of development. I have left in the background the older and the well-tried methods of the last decades; more novel, Utopian proposals I have considered myself justified in excluding.

## APPENDIX (EDITOR'S NOTES)

### (a) *Recent Developments in Low-Temperature Carbonisation.*

THE technique of low-temperature carbonisation has made considerable progress in recent years, particularly in Great Britain. The exaggerated claims for individual types of plant put forward by some of those exploiting inventions in this branch make an unbiased technical judgment somewhat difficult. In view of the national importance of the problem, the Fuel Research Board has been empowered by the Government to make tests at the public expense of plants for the low-temperature carbonisation of coal, with the object of placing in the hands of those interested accurate technical data, but without pronouncing on their commercial possibilities.

The first plant submitted to test under this scheme was the Parker plant, installed at the Barugh (Barnsley) works of Low-Temperature Carbonisation, Ltd. The results obtained and published by the Department of Scientific and Industrial Research <sup>210</sup> may be taken as authoritative, and an abstract of the report is given below. Additional interest is lent to this test in that the plant examined is designed practically on the lines of that originally built by Thomas Parker, the pioneer of low-temperature carbonisation.

Another process which has reached the commercial stage is that of R. Maclaurin. Although this has not yet been submitted to test by the Fuel Research Board, the fact that a large plant under Maclaurin's patents has been erected at Dalmarnock Gas Works by Messrs. Blair Campbell and McLean, Ltd., for the City Corporation of Glasgow justifies the inclusion of its description in these notes.

*Parker Plant.*—The general lay-out of the plant is shown diagrammatically in the drawing (Fig. 73). The pipe lines and recovery plant had not been specially constructed to suit the setting under examination, but had been altered and adapted from the services of a former plant. The setting not in use during the test is shown dotted.

Each setting consists of a battery of 32 retorts, arranged as shown, the off-take pipe of each leading to a hydraulic main running along the side of the setting.

A retort consists essentially of an iron casting in one piece containing 12 vertical tubes arranged as shown in the drawing. These tubes taper from  $5\frac{1}{2}$  inches diameter at the bottom to  $4\frac{1}{2}$  inches diameter at the top, and are 9 feet in length. A special iron swing door, operated by a wheel on the charging platform, closes the bottom of the retort tubes and separates them from a cooling chamber. This chamber is built of brick and one chamber is provided for each pair of retorts. A gas-tight door allows access to this chamber for discharging coke. While the coke is cooling in the chamber any gas liberated is drawn off into a secondary main below the hydraulic main. The gas leaving the system passes through a governor to a condenser (air-

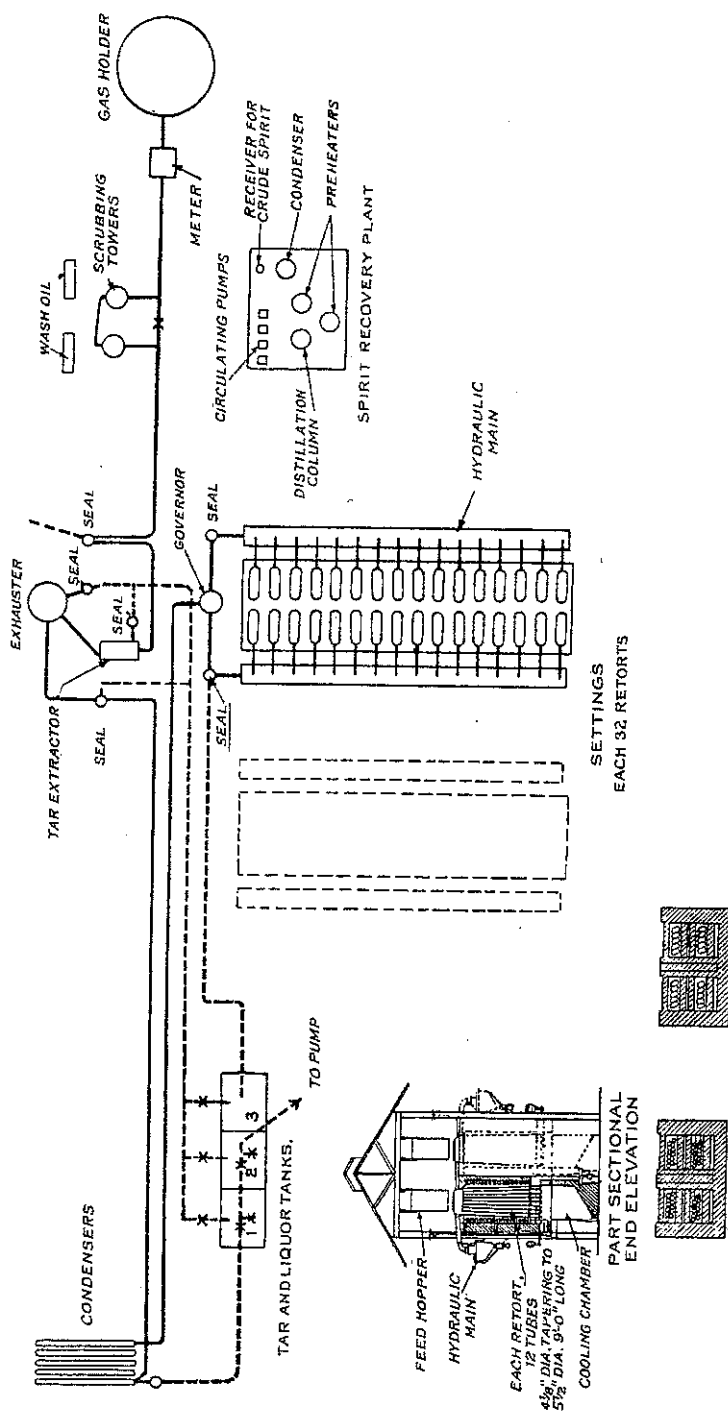


FIG. 73.

cooled), an exhaustor, a tar extractor, an oil-washing plant, a rotary gas-meter and finally to a holder (of 25,000 cubic feet capacity). In this holder it is mixed with producer gas and the mixture used as a fuel gas to heat the settings. Two main seals are provided, one at the end of each hydraulic main, and from these the tar and liquor flow to a collecting tank. The tar and liquor from the condenser and from the seals below the exhaustor and tar extractor flow to a different collecting tank.

A weight balance was prepared and found to show a loss of 0.48 per cent. This, in conjunction with the thermal balance loss of 5.2 per cent., may be regarded as very satisfactory.

The yields of products per ton of coal were as follows:—

Coke . . . . .	13.92 cwts.
Gas . . . . .	5,620 cu. ft. or 39.6 therms
Tar . . . . .	18.62 gallons
Liquor . . . . .	26.00 „
Crude spirit . . . . .	1.78 „
Ammonium sulphate . . . . .	13.55 lbs.

The coke or smokeless fuel produced was of a very suitable size (1 to 3 inch pieces). It was not friable, and contained only 4.6 per cent. of breeze below  $\frac{1}{2}$  inch. Analysis of this coke showed that it contained only 4 per cent. of volatile matter. When burnt in a household grate it was readily ignited and gave a good hot fire.

The yield of tar was high, representing 68 per cent. of that obtained in the assay apparatus.<sup>211</sup> On examination this tar proved to be a normal low-temperature tar.

The yield of gas was fairly high and, throughout the test, varied considerably both in volume and in calorific value owing to variations of pressure in the hydraulic main.

The yield of ammonia was also fairly high. The liquor was, however, less than 6 ozs. strength, and it is questionable whether so dilute a liquor would justify recovery.

The crude spirit obtained by scrubbing the coal gas amounted to 1.78 gallons per ton of coal. The refining figures and distillation range of this spirit are given in the report.

Details are given of the working operations, of the labour and power required, and of a variety of noticeable points in the handling of the setting.

The temperature of carbonisation was not uniform throughout the setting, varying from 600° to as high as 800°. Suggestions are made for the improvement of temperature control. The amount of fuel consumed in the setting was

excessively high, owing to this high temperature, to insufficient heat insulation and to badly designed combustion chambers. There is no doubt but that the 83.5 therms consumed per hour could be reduced considerably.

*Maclaurin's Plant.*<sup>212</sup>—This installation consists of a battery of 5 units, each unit being capable of carbonising 20 tons of coal per 24 hours. The general appearance of the producer unit (see Fig. 74) is somewhat like that of a blast furnace, but it is built square and raised from the ground on piers. The height from charging hoppers to discharging chutes is 36 ft.,

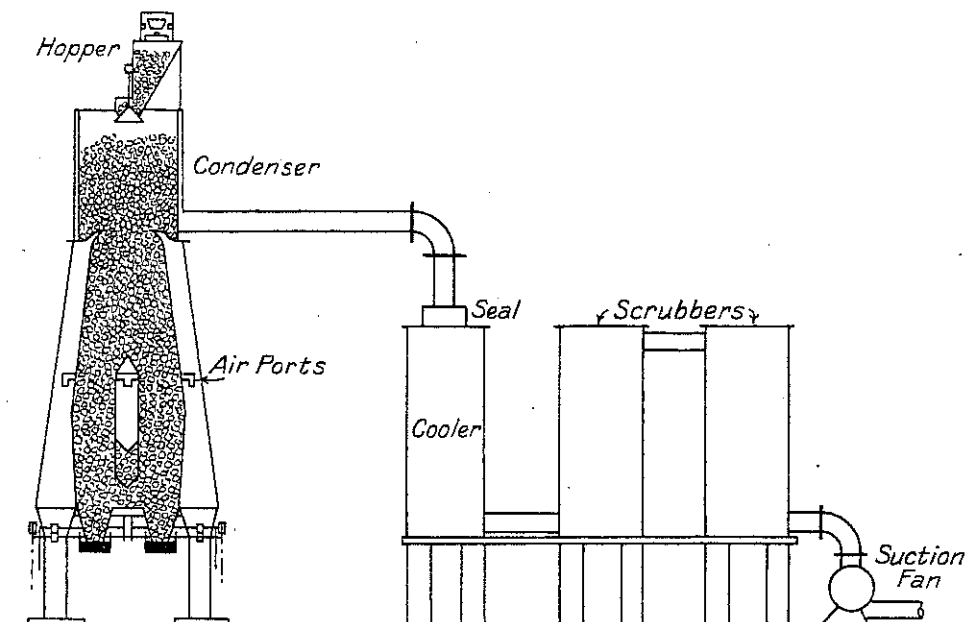


FIG. 74.

and the internal width at the widest point is 8 ft., tapering upwards and downwards.

A centre wall divides the lower portion of the plant into two chambers of equal size. The air enters through ports in the centre and side walls. The coke after cooling is discharged through chutes at the bottom.

In starting up for the first time the producer is filled with ashes to a little above the air ports. Inspection doors at this point are used for lighting up. Through these doors a quantity of wood is inserted and lighted. When properly ignited, the producer is rapidly filled to the top with coke, the air blast being kept going all the time. When the heat has travelled well up the producer, sufficient ash is discharged to permit a ton of coal being dropped in through the bell. Every hour thereafter a discharge is made and approxi-

mately one ton of coal is admitted. After 20 hours the first charge of coal will be approaching the combustion zone, and at from 25 to 30 hours the first coke made from the coal added will be withdrawn.

It has therefore taken 20 hours to raise the coal from 15° to the desired cooking temperature of approximately 700°. The coal descends about one foot and its temperature is raised about 35° per hour. This very gradual increase in temperature is responsible for the production of a coke which is quite different from ordinary gas coke.

The appearance of the coke differs sometimes so little from that of the original coal that it does not seem to have been carbonised at all. Usually, however, the coke is much more open and cellular in structure than the original coal, though its shape has changed very little. The distortion becomes greater the higher the caking index of the coal used. It is hardly correct to term this coke a low-temperature coke, for it has been heated to a temperature well above 600°, and it retains only from 3 to 4 per cent. of volatile matter. It, however, ignites quite readily if the temperature has not been excessive. Maclaurin considers that the ease of ignition is due to the porosity of his coke, and not to the volatile matter remaining in it.

When the temperature is raised beyond a certain degree, a completely different coke is produced. Instead of the black and easily-ignited smokeless fuel, a silvery-grey coke is obtained; its ring when struck is more metallic, its hardness slightly greater and it is not so readily ignited, although the percentage of volatile matter differs so little from the black variety that the ordinary laboratory test fails to distinguish between the two types of coke.

The yield of gas and type of coke produced are interdependent. Black smokeless fuel is produced with a make of gas of between 25,000 and 30,000 cubic feet, and the grey type with a make of over 30,000 cubic feet per ton of coal.

From the Scottish coals tested, which contained from 6 to 10 per cent. of moisture, and from 30 to 35 per cent. of volatile matter, about 55 per cent. of smokeless fuel has been obtained.

Before the coke is withdrawn it has to be cooled, and for this purpose steam is blown in at the discharging chutes. The steam first cools the coke and is then itself decomposed into water gas, as it approaches the combustion zone.

In the combustion zone, air at 60° saturated with water vapour maintains the temperature by burning a portion of the carbon of the coke. The hot producer gas made in this zone supplies all the heat necessary for carbonisation. This gas has a calorific value of about 150 B.Th.U. Above the combustion zone there is a zone where the fuel is between 750° and 500°. Above this is the distillation zone, where the coal is giving off tar and gas. The gas

liberated has a high calorific value, possibly 700 to 800 B.Th.U., but its volume is relatively small. This gas mixes with the producer and water gas made below, and after passing through the coal in the condenser, where much of the tar condenses out, passes down the annular space between the two cylinders and then through the seal and coolers. The calorific value of the combined gases is approximately 240 B.Th.U.

The successful working of the Maclaurin plant is due to the provision made for trapping the condensing tar and preventing it from running into the hotter regions below and thereby suffering decomposition, and eventually causing the coal to be bound together into an impenetrable mass.

Tar with some water collects in the trap where it acts as a seal, passes under the inner cylinder and overflows by the gas main. The gas must, therefore, pass through the cold fuel before it leaves the plant and in so doing is cooled down to about 70°. Little heat is lost, as both gas and coke leave the plant at comparatively low temperatures.

To avoid radiation losses the brickwork is made 18 in. thick, with a special non-conducting brick on the outside, the whole being enclosed in a metal casing. The tar yield is from 14 to 20 gallons, according to the coal used.

Some ammonia is given off in the direct distillation of the fuel, and a further portion is formed by the steam passing through the zone between 750° and 500°. This ammonia is carried forward with the gas, part condenses in the coolers and part is washed out in the scrubbers. The quantity obtained varies from 17 lbs. to 30 lbs. according to the quantity of nitrogen in the coal used. The ammonia liquor differs materially from ordinary gas-works liquor. It contains neither ferrocyanides nor thiocyanates, but a considerable proportion of poly-hydric phenols.

The cooled coke drops into a trolley running below the plant, which is elevated to the top of the coke bunkers of 110 tons capacity. The trolley is emptied on to coke screens, and in this way the coke is divided into three sizes, each size going to its respective bunker. These bunkers lie over the railway, so that wagons can be filled direct from them.

The quantity of ash contained in the coke naturally depends upon the ash contained in the original coal used, but the ash is not equally distributed throughout the different sizes of coke.

When washed trebles are used, the percentage of ash in the coke nuts agrees very closely with that calculated, but when large coal of a low caking index is used, a considerable concentration of the ash takes place in the dust, and frequently in the smaller size of coke. With such coal the large coke is found to be much freer from ash than the other portions.

(b) *Lessing Process for the Separation of Oils and Pitch from Tar.*

For the purpose of recovering the highest possible yield of liquid oils from coal tar and to avoid thermal decomposition upon distillation, Lessing investigated the separation of tars of various character into oil and pitch by means of solvents. The fact that the asphaltic constituents of coal tar are precipitated by petroleum ether was made known as early as 1869 by Jacobsen.<sup>213</sup> He found, however, that the pitch is precipitated together

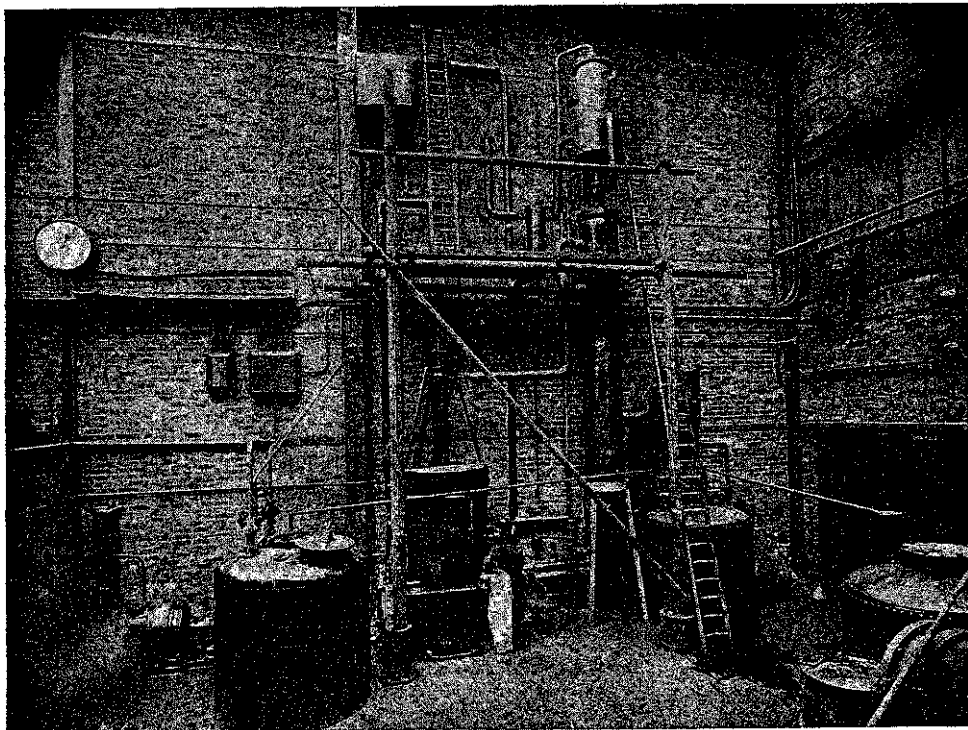


FIG. 75.

with part of the oil, forming a tough mass, which is difficult to handle. Other attempts to remove pitch from tar by means of solvents also failed for lack of sharpness of separation.

Lessing found<sup>214</sup> that a perfect separation could be obtained if coal tar is treated with a non-aromatic hydrocarbon fraction of suitable boiling range at a temperature above the melting point of the pitch to be made and below the initial boiling point of the solvent. He found that coal tars of any description, whether obtained at low or high temperature, in retorts, coke ovens, gas producers or blast furnaces, could be separated at a temperature in the



neighbourhood of 100° into hard pitch and oil. The oil from gas works or coke-oven tar has a characteristic brilliant red colour, similar to that of bromine, and is of low viscosity. Primary tar and other low-temperature tars are of less vivid red or brown colour and, if containing paraffin wax, as in the case of producer or Scottish blast-furnace tars, solidify at room temperature.

One of the main practical difficulties in the substitution of coal tar for natural oil is due to the formation of solid deposits upon mixing or blending them with petroleum or petroleum products. This process provides a means of overcoming this difficulty by the complete removal from the oil of all those compounds which are liable to such precipitation.

Fig. 75 shows a small working unit erected at H.M. Fuel Research Station at Greenwich. The plant is designed on the continuous principle. The tar, from which benzol and naphtha have been removed by "topping," is fed in a steady stream into the extractor, where it is brought into intimate contact with the solvent. Pitch is precipitated instantaneously and is drawn off either continuously or intermittently from the bottom of the extractor. The oil solution passes into a fractionating column charged with Lessing Contact Rings.<sup>215</sup> The oil is completely freed from solvent so as to comply with the British Admiralty specification for flash point, and runs through the bottom outlet into the oil receiver. The solvent vapours are condensed in a reflux condenser and the condensate is returned to the extractor without being cooled below the temperature of condensation, so as to effect the greatest possible heat economy. The temperature differences between any points of the plant are thus reduced to a minimum.

It has been found in practice that the plant can be run with a negligible loss of solvent. In the case of low-temperature tars and any tars practically free from aromatic compounds in their lower fractions, a full yield of spirit boiling below the "cutting" point selected is obtained by passing the excess vapours through a final condenser.

The extraction of tar acids and bases is effected while the oil is still in solution, so that a more rapid and cleaner separation is obtained than in the direct treatment of tar oils.

Table LXXXVII shows the composition of different tars as obtained by Lessing's process.

The principal technical advantage of the process is that it affords a means of obtaining the whole of the oil actually present in the crude tar without loss.

The tar oil can be used directly as fuel oil, Diesel oil or wood preservative. It fulfils the condition of the Admiralty that home-produced oils must be capable of being added to the "common stock," mostly consisting of petroleum oils, without forming any deposits.

On distilling the oil obtained by this process the ordinary range of tar products is obtained. The degree of thermal decomposition can be controlled much easier than in the distillation of crude tar; the process can therefore

be applied with advantage as a preliminary stage in tar distillation, whereby the throughput of a given still capacity is considerably increased, the fire risk is reduced and the burning out of still bottoms is avoided.

TABLE LXXXVII

Type of plant.	Coke oven.	Low-temperature.	Low-temperature.	Mond producer.	Tully producer.	Blast furnace.
Coal used.	Yorkshire.	Lancashire.	Yorkshire.	Staffs.	Scottish.	Scottish.
Neutral oil . . .	54.01	55.98	66.0	36.89	52.07	46.44%
Tar acids . . .	8.18	24.41	17.4	14.36	16.03	29.53 „
Tar bases . . .	—	0.17	—	0.58	1.43	—
Total oil . . .	62.19	80.56	83.4	51.83	69.53	75.97 „
Pitch . . .	37.81	16.96	14.8	48.17	29.20	23.65 „
	100.00	97.52	98.2	100.00	98.73	99.62 „

In addition, the method of separating the tar without subjecting it to the risk of thermal decomposition is of importance for the study of its composition inasmuch as the tar can be subdivided into groups of compounds without secondary change. The difference from the customary examination of tar by distillation becomes manifest from Table LXXXVIII, upon comparing the figures given for free carbon in the pitch from distillation and that obtained on precipitation.

TABLE LXXXVIII

Type of plant.	Horizontal gas retorts.		Vertical gas retorts.	
Coal used.	Yorkshire.	Durham.	Yorkshire.	Durham.
Free carbon in :	%	%	%	%
Pitch from distillation . . . . .	50.15	46.81	52.96	42.24
„ „ Lessing process . . . . .	33.61	34.08	18.38	24.67
Free carbon calculated for dehydrated tar :				
Pitch from distillation . . . . .	30.31	33.17	18.29	17.31
„ „ Lessing process . . . . .	19.78	20.41	5.15	7.16
Found in dehydrated tar . . . . .	19.27	18.78	6.46	6.07

### (c) Hydrogenation of Coal in the Absence of Oil

During the last two or three years a considerable amount of work has been done on the hydrogenation of coal by the Bergius process, as distinct from the hydrogenation or Berginisation of oil, which until then claimed the almost undivided attention of those interested in Bergius' proposals. Of

importance are the papers <sup>216</sup> by Waterman and Kortlandt, Waterman and Perquin, Kling, Bruylants, Erculisse, Shatwell and Graham. Bergius found it necessary to add an oil to the coal, partly in order to treat the coal in a dispersed state and partly in order to simplify the technical procedure. Bergius used for this purpose middle oil, or even coal tar itself. Waterman and his collaborators carried out the Bergius reaction in a medium of paraffin wax, after studying the behaviour of this substance in great detail; Shatwell and Graham employed phenols, which they found to remain unaltered, as was to be expected from Sabatier's researches.

It is not within the scope of this note to examine critically or even summarise the results of these researches; they are merely recorded for ready reference, as additions to the literature since the completion of the German edition.

The most recent publication on the subject is a paper by Franz Fischer and Frey <sup>217</sup>; the interest of their work lies in the fact that they treated various bituminous coals, brown coal and brown coal semi-coke without the addition of an oil of any kind. Bergius had made his preliminary laboratory experiments on coal alone, <sup>218</sup> and Fischer and Frey's results definitely confirmed the possibility of the liquefaction of coal under these conditions.

The coals used were Lohberg gas-flame coal, Osterfeld fat coal, English (Shipley) and Silesian (Lipine) sand (non-caking) coals, Rhenish brown coal and brown coal semi-coke. They found that hydrogenation begins at the same temperature as the formation of primary tar; they concluded therefore that the coal forms primarily gas, water and tar and absorbs hydrogen simultaneously or subsequently. This indicated the way to separate the two phenomena into carbonisation and subsequent hydrogenation of the semi-coke, and also made it desirable, by the use of non-caking coal yielding pulverulent semi-coke, to offer a larger surface to the action of the hydrogen.

In all cases hydrogenation took place, the yield of liquid products varying with the type of coal, the temperature and hydrogen concentration.

The yield of oils is larger than is obtainable by low-temperature carbonisation. The oils obtained are not entirely hydrocarbons, but contain up to 20 per cent. of phenols. The phenols are not those belonging to or derived from the primary tar, for they are also obtained in the hydrogenation of tar-free semi-coke. The following were the yields from brown-coal semi-coke in one of the experiments, showing that it was converted almost entirely into gaseous and oily products, leaving only the mineral matter behind:—

Left in autoclave {	Water . . . . .	40	grams = 8.5%	} 45% oily products.
	Oil distilled off . . . . .	143	„ = 30.0 „	
	Soluble in benzene . . . . .	72	„ = 15.2 „	
	Solid combustible residue . . . . .	29	„ = 6.1 „	
	Ash . . . . .	48	„ = 10.1 „	} 16% solid residue.
	Gas and loss . . . . .	143	„ = 30.1 „	
		475	„	100.0 „

The combined products from three experiments with semi-coke gave a steam distillate which after extracting 13 per cent. of phenols showed the following boiling range:—

75°	110°	120°	130°	140°	150°	160°	170°	180°	190°	200°	210°	225°	230°	240°
Drop	2	4	8	16	24	32	40	44	49	58	68	78	83	80

Non-caking coals (*i.e.*, those containing a large proportion of durain) and semi-coke are more suitable than caking coals. In principle, one may expect corresponding results from the semi-coke of bituminous coals.

The hydrogen balance showing the distribution of the hydrogen used in each experiment, over the water, gas and oil formed gives a telling picture of the hydrogenation process. The tendency is for the hydrogen to form saturated gaseous products, but by judiciously increasing the pressure and reducing the temperature, it is possible to influence the reaction towards the formation of liquid products.

The significance of the sulphur compounds in coal, to which Kling had directed attention, was confirmed and the addition of metallic oxides such as CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, recommended by Bergius seems well justified in this respect.

Fischer and Frey conclude their summary by advising the study of the physical factors controlling the hydrogenation process in addition to its chemistry and expect from this a considerable advance in our knowledge of its mechanism.

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